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VOLUME 10 No. 4

OCTOBER 1956

PERGAMON PRESS · LONDON & NEW YORK

Geochim. et Cosmochim. Acta

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Publishing Offices: Pergamon Press Ltd., 4 & 5 Fitzroy Square, London W.1. (EUS 4455)

Subscription per volume (including postage) (A) £5 10s. (U.S.A. $15.40); (B) For individual subscribers certifying that the journal is for their private use, £3 10s. (U.S.A. $9.80)

Back numbers, £7 ($19.60) per volume

Distributors: I. R. Maxwell & Co., Ltd., 4 & 5 Fitzroy Square, London W.1

and Pergamon Press, Inc., 122 East 55th Street, New York 22, N.Y.

PERGAMON PRESS LTD., 4 & 5 FITZROY SQUARE, LONDON W.1
PERGAMON PRESS, INC., 122 EAST 55TH STREET, NEW YORK 22, N.Y.

Geochimica et Cosmochimica Acta, 1956, Vol. 10, pp. 197 to 223. Pergamon Press Ltd., London

Quantitative spectrochemical analyses of some silicate and carbonate rocks and iron ores with the Stallwood air-jet

J. E. Hawley and Graham MacDonald
Miller Research Laboratory, Queen's University, Kingston, Ontario

(*Received* 8 *December* 1955)

Abstract—The need for ready and rapid techniques for the analyses of a wide range of geological materials has inspired an investigation of the use of the Stallwood air-jet in d.c. arc-spectrochemical determinations of major, minor, and trace constituents.

Techniques have been developed for the analysis of siliceous igneous and metamorphic rocks, carbonates, and ferric-oxide type of iron ores. Basic silicate rocks are still under investigation. The methods expand the use of strontium carbonate as first developed by Kvalheim, but for certain analyses barium carbonate is substituted. For some trace elements, Pd and In are also used as internal standards. Favourable features of the air-jet in eliminating matrix effects, and improving precision and linearity of curves, are illustrated.

For many of the principal constituents of siliceous rocks an error of less than 5% is indicated by comparison of chemical and spectrochemical results on G-1 granite and W-1 diabase and five other rocks. Colorimetric methods for silica and flame photometer, for alkalies, provide useful checks. Spectrographic results on twelve trace elements in G-1 granite and ten in W-1 diabase compare well with determinations given by Ahrens.

For the analysis of basic silicates and for determinations of MgO in carbonates, barium carbonate appears superior to strontium carbonate and is being further developed for the former, but strontium carbonate air-jet methods for analysis of impure carbonates ranging from limestones to dolomites are presented and their relative precision given.

The latter methods are also applicable to ferric-oxide types of iron ores for eight trace elements.

1. Introduction

Within the past ten years several spectrochemical techniques have been described for the analysis of many of the common oxides occurring in silicate and carbonate rocks, and various rock products and minerals. Some of these have been designed to cover ranges in composition limited by the general requirements of the material, as in the case of products used for the manufacture of cements, porcelains, etc., and such products as blast-furnace slags. In some cases the accuracy sought has not been great, as with aluminium ores, where such methods were designed for routine grade-sorting and preliminary testing. For more diverse material, semi-quantitative methods have been described by Waring and Annel (1951), and Ahrens (1954) has indicated the possibility of establishing, through the use of well analysed standards of natural rocks and minerals, more precise methods of suitable accuracy compared with wet-chemical methods.

The advantages of spectrochemical methods in both speed and cost are well recognized, and an investigation of several methods already described has led to an improved technique of good reproducibility and accuracy. This involves the use of strontium carbonate with buffer graphite, a d.c-arc discharge, and the use of an air-jet designed originally by B. J. Stallwood (1954) and modified by Lang and Sturrock (1954) in the spectrographic laboratory, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

The versatility of the method is indicated by its application to the analysis of major and minor constituents of granitic igneous and metamorphic rocks, limestones and dolomites, and of trace elements in iron ores. Difficulty, however,

has been encountered in the analysis of the more basic and hydrous types of igneous and metamorphic rocks with high concentrations of iron, magnesia, and water, but substitution of barium for strontium carbonate overcomes this in part.

Previous Work

Recent texts and papers on spectrographic procedures review various methods for the analysis of rocks and rock products: Ahrens (1954), Churchill and Russell (1945), Coulliette (1943), Fitz and Murray (1945), and others. Kvalheim (1947) first proposed the use of strontium carbonate as an internal standard and buffer for K, Na, Al, Ca, Mg, Fe, and possibly for Mn and Ti, and of beryllium carbonate with sodium chloride for silica. His d.c.-arc method, requiring $\frac{1}{8}$-in. crater electrodes for major constituents and larger ones for minor constituents, yielded a relative error of less than 10% and in some cases less than 5%. High potash (over 8%) was found to affect alumina determinations by as much as 10%, but this was avoided by dilution of one part of sample with five parts of quartz.

Later Dennen, Ahrens, and Fairbairn (1951) employed Kvalheim's method with modifications such as the use of lithium (spodumene) as an internal standard for potash when greater than 3%, and for sodium. For lower concentrations of potash, after determining soda, the latter was used as a variable internal standard against potash. For silica and alumina, high dilutions with graphite were made and beryllium or palladium were used as internal standards. Their results were decidedly encouraging, and in comparison with chemical methods used by seven chemists in one laboratory on specially prepared samples of granite (G-1) and diabase (W-1), they were able to show that spectrochemical methods by two spectrographers were superior to chemical for total iron, MnO, MgO, and CaO (in granite) and Na_2O, and were relatively equal to flame photometric methods for Na_2O; however, the superiority of chemical methods for the major constituents, SiO_2 and Al_2O_3, and of the flame photometer for K_2O, were clearly indicated.

Still other methods for determination of common rock-forming oxides include an interrupted d.c.-arc, platform-electrode technique described by Hasler, Harvey, and associates (1950) for the analysis of cements to which lithium carbonate is added and from which briquettes are prepared. Ranges in composition investigated were however below a maximum of 10%. Applied Research Laboratories (1952) also developed a method for the quanto-metric analysis of iron-alloy slags which seemed to offer interesting possibilities for rocks in which various oxides are present in different crystalline minerals. This involved the fluxing at 1000°C of equal quantities of lithium carbonate and boric oxide with sample and the briquetting of a crushed sample of the resulting glass bead. The method could obviously not be applied to alkalies; and besides, high iron and chromium were found to affect the CaO curve. Application of this method by us for Al_2O_3 in silicate rocks resulted in a very flat curve, using lithium as the internal standard.

Leininger and Taylor (1954) describe a modification of Kvalheim's strontium carbonate method for spectrographic determination of silica, alumina, Ca, Mg, Mn, and thirteen other trace elements in silicate rocks. Alumina and silica are determined from intensity ratio Al/Si by the mutual standard method of calculation. A second method involves mixing with ferric-oxide–palladium, so all final mixtures contain 5% iron which is used as an internal standard.

More recently, Dennen and Fowler (1955), though using d.c.-arc methods on rock samples, followed Coulliette in using the "mutual standard" method of calculation, the accuracy of which depends very closely on the precision and reproducibility of determinations on alumina, the variable internal standard. As our experience in the determination of this particular oxide indicated poor accuracy though at times excellent reproducibility, this method was not considered further, though results show it to be reasonably accurate and rapid.

The beneficial use of air-cooled electrodes for spectrochemical analyses of powders has been described by Stallwood (1954). Although used chiefly for the analysis of minor constituents in highly variable matrices, as described later by Lang and Sturrock (1954), it seemed likely that Stallwood's air-jet should be readily applicable to the analyses of rocks of widely varying composition.

3. Quantitative Methods using the Stallwood Air-jet

Various procedures have been established, using the Stallwood air-jet and d.c.-arc methods for the quantitative analysis of major constituents of siliceous igneous and metamorphic rocks, and of trace elements in these. Though some difficulty has been encountered in similar analyses of more basic, iron-magnesia-rich, and hydrous rocks, some progress has been made, and the technique has also been applied to the determination of both major and minor constituents of carbonate rocks ranging from limestones to dolomites, and of the trace elements in iron ores of the ferric-oxide type.

The air-jet, a detailed description of which is given by Stallwood (1954), is mounted in the arc-spark stand in the same manner as the Petrie stand and is heavily insulated from the base of the instrument. The jet is designed to yield an even upward current of air on all sides of the sample electrode and a minimum of turbulence. Air is supplied from a tank fed by a presso-vac pump, and the air line is connected to a manometer located close to the image of the arc flame. Air-pressure is held at about 9 in. of mercury, but slight departures from this have not proved critical. This pressure prevents flaring out of the arc flame, and yields sharper lines, and, along with the effect of closing down grating doors, aids in reducing cyanogen band spectra and the production of films with essentially no background. Working curves obtained do not indicate that loss of sample by this pressure is important.

The advantages of the air-jet technique emphasized by Stallwood are the elimination of selective volatilization, interference, and other variable matrix effects on the sensitivity of the elements being analysed. A great improvement in linearity is also found in the intensity-concentration curves.

The use of other gases than air to eliminate band spectra, although not thoroughly explored, appears another decided advantage of this equipment.

Procedures and results of quantitative analysis of various rock and mineral types are given in the following sections.

A. *Major Constituents of Siliceous Igneous and Metamorphic Rocks and Minerals*

The method detailed under this heading has been used particularly for siliceous igneous and metamorphic rocks ranging in composition from granite and syenite to diabase, and includes granitic gneisses and feldspars. It cannot be used directly for more basic rocks nor for those containing an abundance of hydrous minerals.

Preparation of sample. Samples of rocks or minerals are first broken down to $\frac{1}{4}$-in. fragments or smaller and then are gradually reduced in size by tamping in a Plattner mortar, and eventually are finely ground in mullite, alumina, or agate mortars, care being taken to avoid metal contamination arising from the use of conventional crushers.

Representative samples are then mixed with strontium carbonate (spectrographically pure grade where trace-element studies are involved), and buffer graphite in the ratio of 1 : 1 : 2. Mixing is carried out on 400-mg lots in an agate mortar to which sufficient methyl alcohol has been added to produce a fluid paste.

Mixing is accomplished with a pestle for 10 to 15 min, and samples are dried below an infra-red lamp and then stored in glass vials.

Spectrographic Conditions

The spectrographic conditions found most suitable with a 2-m grating (24,400 lines per inch) spectrograph and a d.c.-arc discharge from an Applied Research Multisource Unit are as follows:

Time	5-sec pre-burn, 40-sec exposure
Gap	4 mm
Slit	60 microns
Amp	6
Volt	300
Transmission	25%
Grating doors	0·2
Electrodes	Sample $\frac{1}{8}$ in. bored with $\frac{3}{32}$-in. crater, $\frac{1}{2}$ in. deep counter $\frac{1}{8}$ in. sharpened with pencil sharpener
Polarity	Sample positive
Film	Spectrum analysis Film No. 1
Photography and Densitometry	Standard methods used throughout

A.R.L. densitometer and calculating board for determination of intensity ratios.

Electrodes cut in 1-in. lengths are fashioned as noted, and after loading are mounted in brass adapters. The counter electrode is positioned directly above the sample and is collared by the Stallwood air-jet, the upper lip of which is adjusted about 4 mm below the optic axis of the spectrograph so as not to interfere with the photography. As noted above, the air pressure of about 9 in. of mercury is maintained on the air-jet. Although the initiator spark causes a small amount of sample to blow out, a drop of collodion to seal the top of the sample was found to act as an insulator, and, with our equipment, is best omitted. Before starting the discharge, the electrodes are placed very close together, and this, with a 3-to-5-sec pre-burn, overcomes any differences arising from a slight loss of sample. During the exposure a 4-mm gap is maintained by manual controls on the arc-stand columns, guided by the image of the arc obtained by a lens located at the back of the arc-spark stand.

Preparation of Standards

The well-analysed granite (G-1) and diabase (W-1) rocks supplied by the United States Geological Survey, and described in U.S.G.S. Bulletin 980, afforded most useful standards for this work. Suitable mixtures of these gave intermediate compositions, and these were augmented by other rock minerals, glass, and refractories obtained from the United States National Bureau of Standards. These included burnt refractory Nos. 76 and 77, flint and plastic clay, argillaceous limestone, dolomite, soda feldspar, lead-barium glass and opal glass, a list of which with mixtures is given in Table 1.

Samples of these and various mixtures were prepared and analysed according to standard procedures, and working curves were established for each of the major constituents.

Line Pairs and Ranges in Composition for Oxides

As an internal standard Sr 2931·8 was used throughout for all elements except sodium, with which Sr 3366·3 was paired. Element lines used over specified ranges of oxides are given in Table 2.

Table 1. Standards for major oxides in rocks

No.	Material
1	Granite (G-1) (U.S.G.S. Bull. 980)
2	Diabase (W-1)
3	Mixture G-1–W-1 (1 : 1)
4	W-1 plus quartz (1 : 1)
5	W-1 plus quartz (1 : 2)
6	Soda feldspar (N.B.S.) No. 99
7	Plastic clay (N.B.S.) No. 98
8	Flint clay (N.B.S.) No. 97
9	Burnt refractory (N.B.S.) No. 76
10	Burnt refractory (N.B.S.) No. 77
11	Opal glass (N.B.S.) No. 91
12	Obsidian (M.I.T.) R-1580 (U.S.G.S. Bull. 980)
13	G-1 plus potassium carbonate
14	Argillaceous limestone (N.B.S.) No. 1a
15	Argillaceous limestone plus W-1 (1 : 1)
16	Dolomite (N.B.S.) No. 88

Working Curves

Working curves for Al, Fe, Mn, Mg, Ca, Ti, Na, and K are illustrated in Fig. 1. The only one which departs much from unit slope is that for Ti. In all cases numbered samples listed above are used as standards; the strontium lines specified for each element are used to determine intensity ratios.

Table 2

Line	Per cent oxide or metal	
Si-2987·6	30 –70	SiO_2
Al-2568·0	6 –40	Al_2O_3
2652·5	4 –40	Al_2O_3
Ti-3199·9	0·15– 1·5	TiO_2
Fe-2813·3	1·0 – 6	Fe
2929·0	1·5 –10	Fe
Mn-2593·7	0·02– 0·2	MnO
Mg-2779·8	0·4 – 4	MgO
2781·4	2 –22	MgO
Ca-3158·8	0·3 – 6	CaO
3624·1	3 –42	CaO
Na-3302·9	2 –12	Na_2O
3302·3	1 –12	Na_2O
K-4044·1	3 –15	K_2O

Precision or Reproducibility

A comparison of chemical and spectrographic precision for the major constituents of granite (G-1) and diabase (W-1) is given in Tables 3 and 4, regarding these as check standards on the working curves established with other standards

listed. Although the number of analyses made spectrographically is considerably less than chemically, with the exception of silica, discussed later, the standard deviations are comparable in both cases and the relative deviations, C, are better for spectrographic results than for chemical for those oxides present in lower amounts.

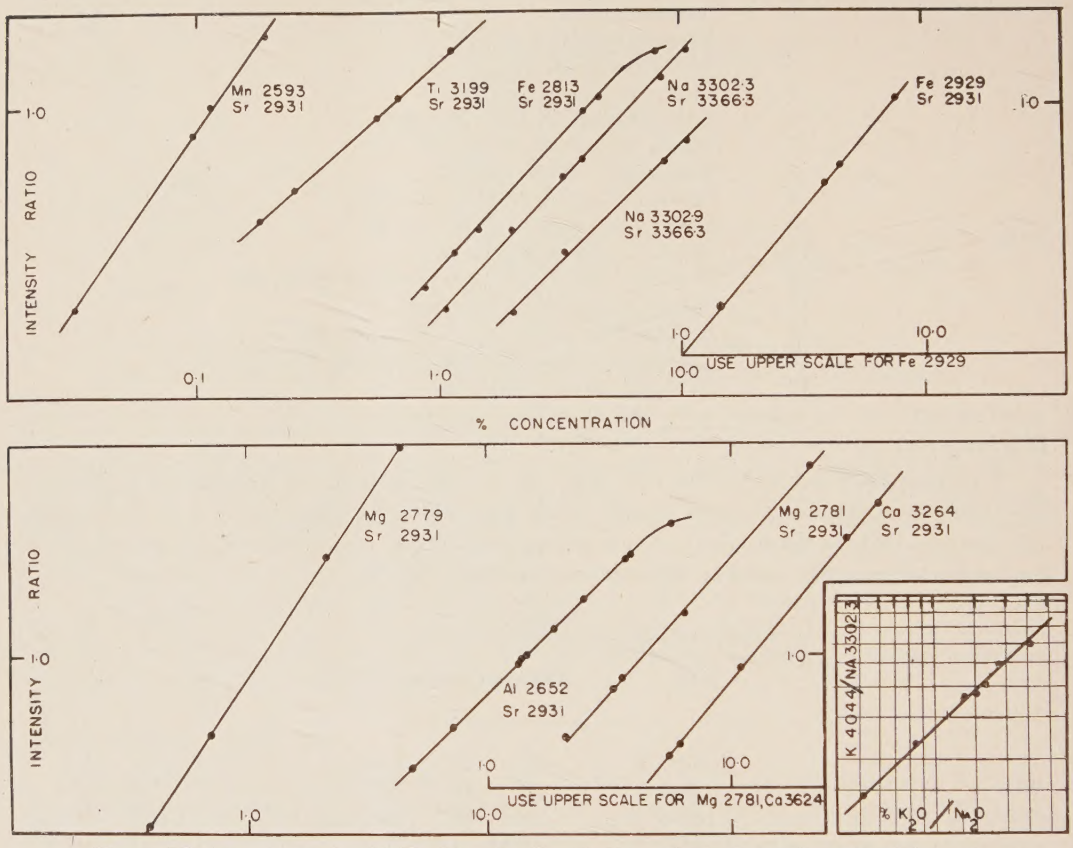
INTENSITY RATIO
Mn 2593 Sr 2931
Ti 3199 Sr 2931
Fe 2813 Sr 2931
Na 3302·3 Sr 33663
Na 33029 Sr 33663
Fe 2929 Sr 2931
USE UPPER SCALE FOR Fe 2929
% CONCENTRATION
Mg 2779 Sr 2931
Al 2652 Sr 2931
Mg 2781 Sr 2931
Ca 3264 Sr 2931
USE UPPER SCALE FOR Mg 2781, Ca3624
K 4044/NA 3302·3
% K2O / % Na2O

Fig. 1. Working curves for Al, Fe, Mn, Mg, Ca, Ti, Na, and K. Intensity ratios Element line/Sr-2931·8, Na-3302·3/Sr-3366·3, in silicate rocks.

Precision on spectrographic determinations of alumina is shown in Table 5 for eight samples, and indicates standard deviations for the most part under 3. This is further discussed under alumina.

Accuracy

As is well known, high precision in spectrographic analyses does not always imply high accuracy. In order to check the accuracy of our methods, five samples of granitic rocks, three analysed by one chemist and two by another, have been analysed by the strontium carbonate-air jet method. In all five cases alkalies have also been determined in our laboratory by flame photometer, and silica by colorimetric methods. In three cases total iron as metallic iron has also been redetermined. The results are given in Table 6, and indicate on the whole a

percentage difference from chemical results, for the more abundant constituents, of less than 10%. The agreement for samples 4 and 5 is particularly good.

In more detail, a discussion of individual oxides is given below.

Silica

A working curve for silica covering the range of 30–70% was established, but as spectrographic errors of even 3–5% allow only an approximation to be made in the higher ranges, the

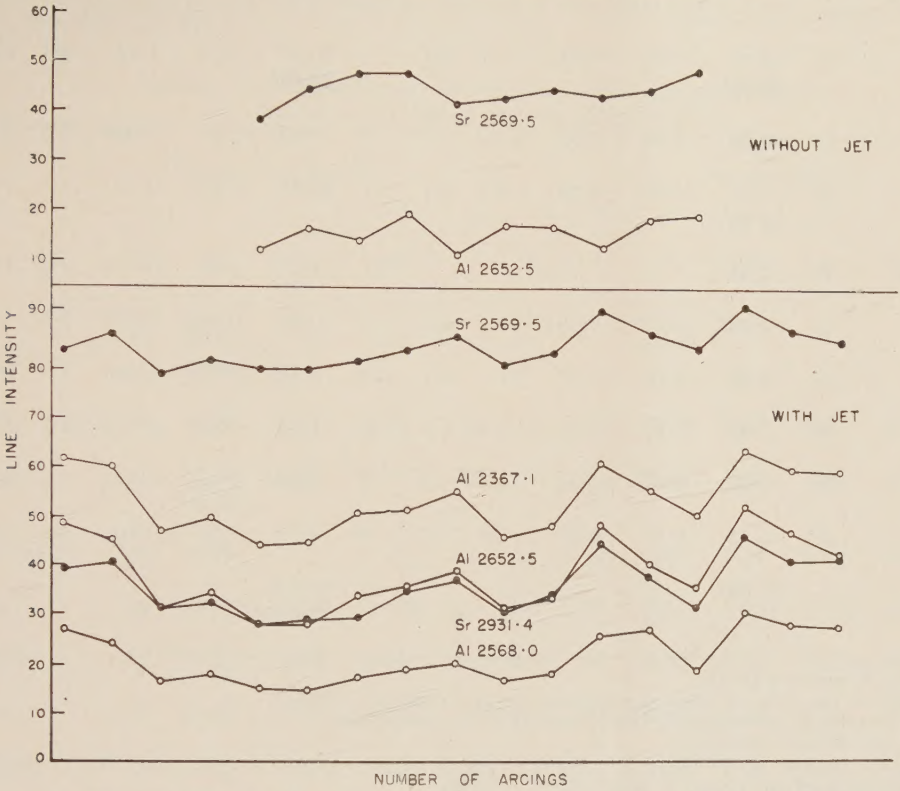

Fig. 2. Line intensities vs. arcing number for Sr and Al, without and with the Stallwood air-jet.

practice of determining silica by the rapid colorimetric method described by Shapiro and Brannock (1952), United States Geological Survey, has been followed. As is evident from Tables 3, 4, and 6, however, a reasonably accurate estimate of silica can be obtained by difference, provided the alkalies are well determined and P_2O_5 and other constituents such as BaO, SrO, H_2O, and CO_2 do not total over 1%.

Titanium Dioxide

The working curve for titanium dioxide covers the range of 0·25 to 1·1% commonly found in granitic rocks. It may readily be extended in both directions by modifying spectrographic conditions. Although the curve departs from unit slope, the accuracy obtained on well-analysed samples is of fairly high order, and in four out of five analyses differences are less than 5%.

Alumina

As earlier investigations of the alumina content of granitic rocks and feldspars, using both nickel and palladium as internal standards, gave erratic results, an intensive study was made of

Table 3. A comparison of chemical and spectrographic precision for the major constituents of granite (G-1)

	Chemical (revised)*						Spectrographic					
	n	$\bar{x}$	s	$s_{\bar{x}}$	C	E	n	$\bar{x}$	s	$s_{\bar{x}}$	C	E
SiO_2	29	72·36 **72·86**[1]	0·35	0·07	0·5	0·1		70·2[2] **72·61**[3]	5·70	1·71	8·1	2·45
TiO_2	24	**0·25**	0·04	0·01	17	3·1	9	**0·25**	0·02	0·008	8·0	2·8
Al_2O_3	28	14·44 **13·94**[1]	0·32	0·06	2·2	0·4	17	**13·98**	0·63	0·18	4·5	1·3
Fe° (calc)	28	**1·41**	—	—	—	—	11	**1·38**	0·04	0·016	3·3	1·2
MnO	27	**0·027**	0·007	0·001	28	5·2	8	**0·03**	0·002	0·001	5·5	1·6
MgO	28	**0·39**	0·10	0·02	27	5·1	14	**0·38**	0·02	0·005	1·4	0·4
CaO	29	**1·41**	0·11	0·02	8·2	1·5	8	**1·40**	0·007	0·024	4·1	1·9
Na_2O	28	**3·25**	0·17	0·03	5·2	1·0	7	**3·26**[4]	0·035	0·013	1·1	0·4
K_2O	28	5·42	0·37	0·07	6·8	1·3	9	5·70	0·32	0·10	5·6	1·9
Total		98·987						96·58[2] 98·987[3]				

* After Fairbairn (1953).
[1] Preferred estimate for silica and alumina (after Fairbairn, 1953).
[2] Per cent silica, spectrographic and total with this percentage.
[3] Per cent silica by difference.
[4] Na_2O = 3·26 on seven of fourteen analyses; overall average of fourteen gives Na_2O = 3·29%; accuracy good but precision poor with C = 25·76.

n—number of analyses; $\bar{x}$—arithmetic mean; s—standard deviation; $s_{\bar{x}}$—standard error (error of arithmetic mean); C—relative deviation, coefficient of variation; E—relative error

this oxide, using strontium carbonate with and without the air-jet. Fig. 2 shows the excellent behaviour of Sr with respect to Al for several lines of each, particularly with the air-jet, on ten or more individual arcings.

As noted above, Table 5 indicates the precision obtained on replicate analyses of eight samples, varying in Al_2O_3 from 4·8 to 58%. Except for the two samples highest in alumina the standard deviation is less than 1, and, in all cases, is less than 3. Attention is called particularly to the results on forty-four analyses of soda feldspar No. 99.

In four of five rock analyses given in Table 6, differences obtained for alumina spectrographically compared with the chemical results are less than 5%.

Iron Oxide

Iron is determined spectrographically as total metallic iron, and has been calculated as such from oxides of analysed standards. The range covered is from 1·0 to 10·0%, but this has since been extended down to 0·04%.

The determination of ferrous iron must be made chemically.

In five analyses of rocks, Table 6, the percentage difference or bias in terms of the chemical determinations is less than 5% in four out of five cases. In fifteen other analyses of granitic rocks, the percentage difference is 6·1%.

Mno, MgO, CaO

Ranges covered by working curves for these oxides are those commonly found in granitic, and even more basic rocks in the case of MgO. Available standards for CaO were limited to three samples, and the accuracy of determinations of this oxide appears to be somewhat poorer than for MnO and MgO.

Table 4. A comparison of chemical and spectrographic precision for the major constituents in diabase (W-1)

	Chemical (revised)[1]						Spectrographic					
	n	$\bar{x}$	*s*	$s_{\bar{x}}$	*C*	*E*	*n*	$\bar{x}$	*s*	$s_{\bar{x}}$	*C*	*E*
SiO_2	32	52·34 52·69*	0·32	0·06	0·6	0·1		53·76[2]				
TiO_2	31	**1·10**	0·15	0·03	14	2·4	9	**1·10**	0·06	0·02	5·5	1·8
Al_2O_3	32	15·07 **14·72***	0·50	0·09	3·3	0·6	10	**14·78**	0·49	0·14	3·3	1·0
Fe° (calc)	30	**8·20**					9	**7·60**	0·72	0·23	9·5	3·0
MnO	32	**0·165**	0·034	0·006	21	3·7	10	**0·15**	0·005	0·002	3·7	1·2
MgO	32	**6·63**	0·28	0·05	4·2	0·7	12	**6·20**	0·02	0·006	0·3	0·1
CaO	33	**10·96**	0·19	0·03	1·8	0·3	10	**10·90**	0·63	0·20	5·8	1·8
Na_2O	32	**2·00**	0·19	0·03	9·3	1·6	10	**1·98**[3]	0·65	0·21	32·3	16·3
K_2O	32	0·63	0·15	0·03	23	4·1		*nd*[4] (0·63)				
Total		97·095*										

* Preferred estimate for SiO_2 and Al_2O_3.
[1] After Fairbairn (1953).
[2] Silica by difference.
[3] Na_2O in ten of fourteen analyses. Average per cent Na_2O in all fourteen = 1·92, but precision is then poor with $C = 20·5$.
[4] $K_2O = 0·63\%$ chemical, not determined spectrographically.

Soda

Determinations on soda have been made both by flame photometric and spectrographic methods on nineteen samples of granitic rocks. For thirteen of these, flame photometric determinations were made both by the Ontario Department of Mines and ourselves. Chemical determinations are also available for five of the samples by other chemists. Though six of the

samples show differences of over 5% of the average flame or other determinations, the overall average of differences between these and spectrographic results is 5·5%. For thirteen samples, however, the average difference is only 2·2%. It thus appears wise for accuracy to continue making flame determinations as well as spectrographic.

Potash

An attempt has been made to determine potash, using lines available in the ultra-violet in order to avoid the necessity, with our equipment, of changing film-type and developing solutions. Although a suitable working curve was established by the use of three standards, the range extends down to only about 3% K_2O, and the curve is not applicable to rocks with lower amounts of this oxide. As results using the intensity ratios of K-4044·1/Sr-2931·8 are not consistently good, the method suggested by Ahrens (1954, p. 56) of using sodium as a variable internal standard has been used with better success, utilizing, however, the intensity ratio K-4044·1/Na-3302·3 against concentration K_2O/concentration Na_2O. Results for potash in granitic rocks of Table 6 were obtained in this manner.

Table 5. Precision of determinations of alumina in various samples

Sample	Per cent Al_2O_3		n	s	$s_{\bar{x}}$	C	E
	Chem.	Spec.					
Diabase W-1 : Quartz 1 : 2	4·91	4·8	9	0·44	0·15	9·00	2·98
Diabase W-1 : Quartz 1 : 1	7·36	7·3	8	0·37	0·13	5·03	1·79
Granite G-1	13·94	13·9	12	0·66	0·19	4·75	1·37
Diabase W-1	14·72	14·8	12	0·47	0·14	3·20	0·91
Soda Spar No. 99	19·06	19·3	44	0·64	0·099	3·31	0·50
Plastic Clay No. 98	25·54	25·0	14	0·62	0·17	2·46	0·64
Flint Clay No. 97	38·77	38·8	12	1·35	0·39	3·50	1·00
Alumina Ref. No. 77	59·4	58·4	10	2·99	0·94	5·82	1·61

Samples 1–4: Analyses of diabase W-1 and Granite G-1 (U.S.G.S. Bull. 980).
Samples 5–8: National Bureau of Standards samples.

n number of analyses
s standard deviation
$s_{\bar{x}}$ standard error
C relative deviation $s/x\%$
E relative error $s_{\bar{x}}/\bar{x}\%$

Summary

Spectrographic determinations of the principal oxides in siliceous (granitic) igneous and metamorphic rocks, employing strontium as an internal standard and the Stallwood air-jet, indicate an accuracy of close to 5% for the constituents present in larger amounts and a suitable accuracy for others. On dried and ignited samples, thus eliminating H_2O and CO_2, silica can be determined reasonably well by difference, but in general practice a colorimetric check determination is made for this oxide in all highly siliceous rocks. Analytical lines used are all within the ultra-violet range and can be read from one film after arcing under one set of conditions.

B. *Trace Elements in Granitic Rocks*

The favourable features of the Stallwood air-jet noted in determinations of major constituents of granitic rocks have been found equally useful in trace-element determinations for these rocks. Amounts of trace elements in many

granites studied vary greatly from several hundred parts per million to one or two, and no one set of conditions will cover such ranges.

Accordingly, four different procedures have been developed, one using potassium sulphate and buffer graphite, and three using strontium carbonate in varying proportions to sample and graphite.

Preparation of Sample

Special precautions are needed in preparing samples for trace-element determinations, as grinding hard siliceous rocks in conventional crushers and pulverizers contaminates the rock with many of the ferride elements. A ready method of disintegrating rocks such as granite is to heat-treat $\frac{1}{2}$-in. specimens in an electric furnace to 600°C, and to quench them in distilled water. After one or more such treatments, and drying, samples of granite may be easily pulverized and finely ground in agate or mullite mortars. Similar treatment of syenitic rocks has been found to render them more brittle and allows easier grinding in mortars.

Finely-ground samples are then mixed with either potassium sulphate or strontium carbonate and graphite in the proportions used for standards. Moisture determinations are made on original rock samples, but in the case of granitic and syenitic rocks the amounts are seldom enough to affect the trace-element determinations an appreciable amount.

Spectrographic Methods

1. *Potassium sulphate*—Potassium sulphate is used with buffer graphite after the method described by Lang and Sturrock (1954), but in lower proportions in order to avoid undue dilution of samples. The ratio of sample to potassium sulphate to buffer graphite used is 1 : 1 : 2.

As an internal standard, palladium is added in solution and mixed with potassium sulphate in the proportion of 10 mg Pd to 50 g salt. Indium is added for the same purpose, but to graphite in the oxide form in the proportion of 1 mg In_2O_3 to 50 g. Pd-3460·8 is used as an internal standard for Ba, Be, Cr, Co, Mn, Mo, Ni, Sr, V, and Zr, and In-3256·1 for Ag, Cu, Li, Pb, and Sn. Our present practice is to use this method only for the determination of Ba, Sr, and Pb, though it may be used at any time as a check on strontium-carbonate methods described below.

As a base for these and other standards a muscovite granite (T-3) from Preissac township, Quebec, was used, as it was found to be particularly low in several trace elements; and amounts of such elements as were detected in it were determined by the addition method (Harvey, 1950). This granite showed no detectable Cr, Co, Mo, or Ni. The addition method indicated the following present in p.p.m.: Ba 35, Be 2, Cu 1·5, Mn 200, Pb 20, Sr 35, V 7, and Zr 40.

Trace elements were added to this base as spec-pure oxides for the refractories, and as solutions for the volatiles,* and desired concentrations were obtained by successive dilutions with the base. Lines used and ranges covered are given in Table 7. Spectrographic conditions used are in general similar to those described for major constituents, but differed from these in the following respects: time, 90 sec; gap, 4 mm; trans., 100%; grating doors, 0·4; $\frac{1}{8}$-in. electrodes with crater, $\frac{5}{64}$-in. dia., $\frac{1}{2}$ in. deep.

Working curves close to unit slope were obtained in all cases and reproducibility tests indicated an overall average relative deviation of 11·5% with a range from 5 to 20%. The accuracy of this method is considered later.

2. *Strontium carbonate* (1 : 1 : 2 *mixture*)—In order to save time on mixing of samples, the same mixture used for determination of major constituents in granitic rocks was tried for their trace elements, that is 1 of sample to 1 of $SrCO_3$ to 2 of graphite. With the exception of Sr, Ba, and Pb, this method has been found very suitable, provided the amounts present are for the most part above 10–20 p.p.m.

Standards used are the same as prepared for the potassium sulphate method, i.e., muscovite-granite (T-3) base to which known amounts of oxides or solutions were added. These and

* Solutions of volatiles were prepared by W. L. Ott, chemist.

analytical samples are mixed with spec-pure strontium carbonate and buffer graphite in the 1 : 1 : 2 ratio and are loaded in $\frac{1}{8}$-in. electrodes with craters drilled to $\frac{3}{32}$-in. dia. and $\frac{1}{2}$ in. deep to give a very thin wall. Discharge is a 9-amp arc, time 60 sec with 3-sec preburn, slit 40 μ, transmission 80%, and grating doors set at 0·2.

For Cu and Pb determinations it was found useful to add indium to the graphite in the form of In_2O_3 and in the amount of 50 mg to 50 g of graphite. In-3258·6 was used as an internal standard for these two elements and for all the others, Sr-2428·1 was found of suitable density to yield satisfactory intensity ratios. Table 7 gives analytical lines and ranges used.

Table 6. Comparison of chemical and spectrographic analyses of granitic rocks

	Chem.	Miller* chem.	Spec.	Diff.	% Diff.
Sample 1					
SiO_2	72·78	70·8	71·00†	1·78	2·4
TiO_2	0·18		0·18	0·0	0·0
Al_2O_3	14·56		15·20	0·64	4·3
Fe°	1·64		1·70	0·06	4·0
MnO	0·02		0·02	0·0	0·0
MgO	0·92		0·92	0·0	0·0
CaO	1·73		1·9	0·17	9·8
Na_2O	3·55	(4·34)	4·5	0·95 (0·16)	26·8 (3·7)
K_2O	2·94	3·21	2·9	0·04 (0·31)	1·4 (9·7)
Total	98·32		98·32		
Sample 2					
SiO_2	74·15	73·14	73·20†	0·95	1·3
TiO_2	0·26		0·25	0·01	3·8
Al_2O_3	12·92		12·9	0·02	0·15
Fe°	1·60		2·1	0·5	31·2
MnO	0·03		0·02	0·01	33·0
MgO	0·37		0·32	0·05	13·5
CaO	0·52		0·56	0·04	7·3
Na_2O	3·38	(3·96)	4·7	1·32 (0·74)	39·0 (18·5)
K_2O	5·21	(5·89)	5·04	0·17 (0·85)	3·3 (14·3)
Total	98·44		98·44		
Sample 3					
SiO_2	51·54	56·62	55·02†	3·48	6·7
TiO_2	0·18		0·13	0·05	27·8
Al_2O_3	24·13		22·6	1·53	6·3
Fe°	4·08	4·12	4·25	0·18	4·4
MnO	0·15		0·09	0·06	40·0
MgO	0·43		0·38	0·05	11·6
CaO	8·96		7·10	1·86	20·8
Na_2O	5·70		5·60	0·10	1·76
K_2O	0·72	0·99	*nd* (0·72)		
Total	95·89		95·89		

Table 6—*continued*

Sample 4

	Chem.	Miller* chem.	Spec.		Diff.	% Diff.
SiO_2	70·73	70·58		70·72†	0·01	0·01
TiO_2	0·44		0·42		0·02	4·5
Al_2O_3	14·29		14·20		0·09	0·63
Fe°	2·21	2·23	2·22		0·01	0·5
MnO	0·04		0·05		0·01	25·0
MgO	0·64		0·65		0·01	1·56
CaO	1·50		1·46		0·04	2·67
Na_2O	2·54	2·67	2·66		0·12	4·7
K_2O	6·55	6·57	6·48	(6·56)†	0·09	1·4
Total	98·94			98·94		

Sample 5

SiO_2	61·69	61·68		61·71†	0·02	0·03
TiO_2	1·06		1·08		0·02	1·9
Al_2O_3	16·02		16·0		0·02	0·12
Fe°	6·16	6·43	5·89		0·27	4·4
MnO	0·08		0·09		0·01	12·5
MgO	2·87		2·80		0·07	2·44
CaO	2·08		2·29		0·21	10·1
Na_2O	2·77	2·82	2·87		0·10	3·6
K_2O	2·54	2·51	2·49	(2·52)	0·05	2·0
Total	95·27			95·27		

* Miller Laboratory chemical determinations:—
SiO_2, Fe°, colorimetric; alkalies—flame photometer.
Fe°—total as metallic iron.

† Silica by difference, using chemical analyses for K_2O in samples 3, 4, 5.

Sample 1—No. 102 White Lake Granite, Black Bay Area, Sask. W. H. Herdsman, analyst (W. E. Hale, unpub. Ph.D. thesis, Queen's University).

Sample 2—No. 221 Red Granite, Black Bay Area, Sask. W. H. Hersdman, analyst (W. E. Hale, unpub. Ph.D. thesis, Queen's University).

Sample 3—K.L.5 Oligoclase-andesine gneiss, Craigmont area, Renfrew Co., Ontario. W. H. Herdsman, analyst (H. D. Carlson, Ont. Dept. Mines, XLII, Pt. 5, Appendix A, 1953, p. 107).

Sample 4—A-3 Metamorphic Granite, Geol. Surv. Canada, Mineral Div., J. A. Maxwell, analyst.

Sample 5—A-19 Granitized rock, Geol. Surv. Can., Mineral Div., J. A. Maxwell, analyst.

Working curves close to unit slope over the ranges indicated were obtained, and reproducibility tests on ten samples of one standard gave relative deviations (C) for Be, Mo, V, Zr, Ni, Cr, and Co of 3, 4, 7·8, 6·5, 4·5, 5·9, and 3·3%, and relative error (E) of 1 to 2·5%.

As for the potassium-sulphate method, a measure of accuracy is given later by analyses of the granite, G-1, page 213.

3. *Strontium carbonate* (8 : 1 : 4 *mixture*)—As analyses of several Precambrian granites made with curves established, as above, showed still lower amounts of several trace elements, an endeavour was made to avoid the dilution entailed by these methods as much as possible. Of various mixtures tried, one of 8 of sample to 1 of $SrCO_3$ to 4 of buffer graphite yielded the most satisfactory results, and samples could be burned to completion without the formation of refractory glass beads.

The 9-amp d.c.-arc discharge was used, and samples were burned for 2 min in $\frac{1}{8}$-in. electrodes with $\frac{5}{6}\frac{5}{4}$-in. craters, $\frac{1}{2}$ in. deep, with slit set at 40 μ, grating doors at 0·2, and transmission 100%. Otherwise, conditions are as for major constituents.

With this discharge, Sr-2569·5 is used as an internal standard line for Be, Co, Cr, Mo, Ni, and V, the lines and ranges of which are given in Table 7.

A reproducibility test on G-1 granite (U.S.G.S. Bull. 980) on thirteen analyses gave the Co content as 0·00022%, a standard deviation of 0.000025, the relative deviation (C) of 11·35% and relative error (E) as 3·44. Accuracy is discussed below. The method appears suitable for the lower ranges of trace elements down to the limits of sensitivity.

4. *Strontium carbonate* (8 : 1 : 0 *mixture*)—To increase sensitivity of the volatile elements and also avoid dilution, a mixture of 8 of sample to 1 of $SrCO_3$ with no graphite was tried on the same sets of standards prepared in the granite (T-3) base.

To the $SrCO_3$, In_2O_3 is added in the ratio 10 of carbonate to 1 of oxide, and the line In-2753·9 is used as an internal standard for Ag, Cu, Pb, and Sn over the ranges shown in Table 7. Electrodes with craters $\frac{5}{6}\frac{5}{4}$-in. dia. are again used with a 6-amp d.c.-arc discharge for 75 sec, with slit at 30 μ, gap 3 mm, transmission 100%, and grating doors at 0·45. Films with practically no background and no cyanogen bands are obtained, and greater sensitivity is gained.

With this technique, glass beads containing the more refractory elements remain in the crater, but time-intensity studies indicate that most if not all of the volatiles are distilled off within 75 sec.

A reproducibility test made on ten samples of one standard (T-3 granite to which 4–10 p.p.m. Ag, Cu, Pb, Sn, Li had been added) gave the following relative deviations (C)—Ag 2·47%, Cu 5·6%, Pb 3–4%, Li 8.3%. These were made all on one film. A similar test on G-1 granite containing about 20 p.p.m. Pb and 11 p.p.m. Cu, gave on twelve analyses relative deviations (C) of 12%.

Accuracy

As a measure of the accuracy of the above methods of analyses, data on trace elements, found in the G-1 granite and W-1 diabase (Ahrens, 1954) are given in Table 8. These are compared with recommended values given by Ahrens and also the ranges of quantities found by eight other analysts.

In spectrographic determinations, aside from errors in the spectrographic and photographic techniques involved, which at best may range from 3 to 5 or more per cent, systematic errors may be introduced by traces of various elements in even spectrographically-pure electrodes, buffer graphite, and other buffers such as, in this case, potassium sulphate or strontium carbonate. The latter may be insignificant when amounts present in the sample are in the tens or hundreds of parts per million, but are important when only a few parts per million are indicated, as of Be, Co, Cu, and Ni in granite. Qualitative tests on potassium sulphate and "spectrographically pure" strontium carbonate show that the former contains no detectable amounts of the trace metals, and that in the latter only minor Ba, Fe, and Cu are present.

Also important when very small quantities are being determined is the effect of an invisible background, as mentioned by Ahrens (1954, p. 15) and indicated in this work in the case at least of Co and Pb, as described below. This effect may also account to some extent for differences obtained for other elements.

In the case of Cu the amount indicated in our base standards by our working curves for the 8 : 1 : 4 mixture of T-3 muscovite granite with strontium carbonate

and graphite, is 1·5 p.p.m., but in the 1 : 1 : 2 mixture, 11 p.p.m. were obtained. This indicates that most of the copper in this case is present in the strontium carbonate, and on this basis 10 p.p.m. Cu have been deducted from the results obtained for the G-1 granite and W-1 diabase.

Similarly the working curves for cobalt in the 1 : 1 : 2 mixture with strontium carbonate and for lead in the 8 : 1 : 0 mixture toe off in the lower concentrations and indicate a residual effect, possibly invisible background (Ahrens 1954, p. 15), equal to about 7 p.p.m. Co, and about 20 p.p.m. Pb, respectively. If this amount of cobalt is deducted from 9 p.p.m. indicated in the G-1 granite, 2 p.p.m. Co agrees exactly with the value recommended by Ahrens. A similar deduction for lead gives a value of 20–24 p.p.m., which is close to Ahrens's value of 27 p.p.m.

As set out in Table 8, rather good agreement is shown between our results for Ba, Cu, Cr, Mo, Pb, and Zr, by the sulphate method and the recommended values for G-1 granite and for Cr, Ni, Pb, and V in W-1 diabase. The result for Ba in the diabase is low, and for Sr in both granite and diabase is high, but all are still within the range shown by other analysts.

By the $SrCO_3$ methods, good agreement is also indicated for Be, Co, Cu, Cr, Ni, Mn, V and Zr in G-1, and for Co, Cr, and Ni in W-1, while results for Cu and V

Table 7. Trace-element methods for siliceous rocks

Potassium sulphate			Strontium carbonate					
			1 : 1 : 2		8 : 1 : 4		8 : 1 : 0	
Element	Line/*I.S.*	Range p.p.m.	Line/*I.S.*	Range p.p.m.	Line/*I.S.*	Range p.p.m.	Line/*I.S.*	Range p.p.m.
Ag	3280·7/In	4–60					3382·9/In	2–200
Ba	4554·0/Pd	50–600					3280·7/In	1–200
Ba	2335·3/Pd	400–1200						
Be	3130·4/Pd	10–150	2348·6/Sr	3–150	2348·6/Sr	3–20		
Co	3453·5/Pd	10–100	3453·5/Sr	12–250	3453·5/Sr	3–40		
Cr	4274·8/Pd	10–100	4254·3/Sr	10–100	4254·3/Sr	3–40		
Cu	3273·9/In	5–100	3273·9/Sr	10–100			3273·9/In	1·5–30
Cu			3247·5/In	5–50			3247·5/In	
Li	3232·6/In	500–1000?						
Mn	3460·3/Pd	250–1500?						
Mo	3170·3/Pd	20–300	3170·3/Sr	5–150	3132·6	3–100		
Ni	3414·7/Pd	10–260	3414·7/Sr	10–300	3414·7	3–50		
Pb	3683·5/In	6–100					3683·5/In	14–15
							4057·8/In	
Sn	2839·9/In	100–400					3175·0/In	10–20
Sr	3464·5/Pd	100–1200						
V	3184·0/Pd	10–200	3184·0/Sr	10–200				
Zr	3438·2/Pd	70–1000	3391·9/Sr*	20–700				

* Zr-3391·9 not suitable with high iron samples.

in W-1 are somewhat high. (High V in W-1 diabase may possibly be due to some enhancement by Ca (Ahrens, 1950, p. 221). Agreement in amounts of elements such as Be, Co, Cr, and V, in G-1, in different mixtures of strontium carbonate, is also of a high order. Results for Cu by the 8 : 1 : 0 method agree exactly with the recommended value for this element, and lead values check those obtained by the sulphate method.

Three different methods, including X-ray fluorescence, give identical values for Zr in the G-1 granite.

To illustrate further the accuracy and versatility of the strontium carbonate air-jet method (1 : 1 : 2 mix), an analysis was made on plastic clay, No. 98 of the United States National Bureau of Standards for ZrO_2 and V_2O_5, using established curves. This clay contains 59·11% SiO_2, 25·54% Al_2O_3, and 3·45 combined alkalies, and is thus comparable with siliceous rocks in these elements. The results are as follows:

	Plastic Clay No. 98	
	Chemical	*Spectrographic*
ZrO_2	0·04%	0·046%
V_2O_5	0·025%	0·029%

C. *Basic and Hydrous Silicate Rocks and Minerals*

Attempts to apply the method used for siliceous rocks directly to rocks and minerals containing appreciable quantities of magnesia, lime, iron oxide and water have so far not proved very successful.

In the first place, rocks containing hydrous silicates such as micas, chlorite hornblende, epidote, and serpentine, unless first calcined to remove combined water or hydroxyl, blow out of the crater, causing rapid loss of sample. Several of these minerals contain a considerable amount of ferrous oxide, and they are not infrequently intergrown with carbonates. Hence, both FeO and CO_2 must be determined chemically. Highly refractory minerals such as garnets and spinels may be also present with such minerals and affect their arcing. The presence also of appreciable amounts of iron oxide and magnesia in such mixtures appears also to change the slope of working curves established on more siliceous rocks, at least for certain line pairs, and accordingly new standards and spectrographic conditions are required for the analyses of such rocks and minerals.

Some such standards have been made available through the kindness of Dr. G. M. Friedman, formerly of University of Cincinnati, in the form of amphibolitic metamorphic rocks analysed under the direction of Dr. S. S. Goldich, University of Minnesota. Spectrographic analyses of these by the method used for siliceous rocks gave very poor results. Using these rocks as standards with strontium carbonate and graphite gave a very steep working curve for Fe-2813·1/Sr-2931·4 and rather flat curves for Al-2652·4 and Na-3302·3. Experiments were then made substituting barium carbonate for strontium carbonate, and curves close to unit slope were obtained for Al, Fe, Mg, Ca, and Na, plotting intensity ratios of Al-2652·5, Fe-2813·1, Mg-2781·4, Ca-3624·2, and Na-3302·3, to Ba-2634·8 in all cases, against concentration.

Table 8. Trace elements in granite (G-1) and diabase (W-1)
Determined by various methods and analysts
(parts per million)

Element in rock	Recommended values (AHRENS, 1954)	Range by eight analysts (AHRENS, 1954)	Stallwood air-jet			
			Potass. sulph.	$SrCO_3$ 1 : 1 : 2	$SrCO_3$ 8 : 1 : 4	$SrCO_3$[d] 8 : 1 : 0
Ba, G-1	**1300**	1100–3000	**1340**			
W-1	270	150–390	190			
Be, G-1	(2)	2–<15		<6	**4**	
Co, G-1	(4)	<2–10		(2)[a]	**3**	
W-1	**36**	20–55	(61)	**43**		
Cr, G-1	**20**	8–30	27	17	**19**	
W-1	**130**	100–150		**116**		
Cu, G-1	**11**	5–20	17[a]	16		**11**
W-1	**110**	44–130		**160**		
Mn, G-1	**210**			**220**		
Mo, G-1	**5·5**	<4–14	**4**	9		
W-1	(0·5)	*nd*4–5		*nd*		
Ni, G-1	(**5**)	<2·5–60	*nd*	<13	(**3·4**)	
W-1	**90**	47–150	120	**102**		
Pb, G-1	**27**	14–50	**21-23**			**20–24**
W-1	7	5–20	<10			
Sr, G-1	280	120–900	440			
W-1	290	120–450	400			
V, G-1	**18**	8–26		**19**	**16**	
W-1	**240**	170–340	**260**	310		
Zr, G-1	**200**	130–280	**220**	**220**[b]		
W-1	90	50–150	(*c*)	30?		

[a] Corrected for invisible background or traces in $SrCO_3$.
[b] Zr–G-1—X-ray fluorescence method—220 p.p.m.
[c] Zr–W-1—Zr not determined due to iron interference.
[d] No detectable Sn, Zn, or Li.
Quantities showing best agreement appear in heavier type.

Ratio of sample to $BaCO_3$ to graphite is 1 : 1 : 2, and spectrographic conditions are as follows: preburn 3 sec, arc 40 sec, 9 amp, gap 3 mm, slit 50 μ, transmission 20%, grating doors 0·2.

Ranges of concentrations covered so far are:

Al_2O_3	10	–25%
Fe	5	–10%
MgO	4·5	–25%
CaO	5·5	–12%
Na_2O	2	–5%

As a check on this method, a sample of chlorite schist, analysed chemically by J. A. Maxwell, Mineralogy Division, Geological Survey of Canada, was run by the barium carbonate–air-jet method, and for three major constituents gave the following results (Table 9):

Table 9. Partial analysis of chlorite schist

	Chem.	Spec.
Al_2O_3	12·56	12·48
Fe	9·33	9·23
MgO	5·04	4·89

These are sufficiently close to suggest the method has some merit, and further work is in progress.

A reproducibility test made on fifteen samples of W-1 diabase for Al/2652·5/Ba-2634·8 at two different times, a month apart, give identical intensity ratios.

As will be shown later, a similar method of analysis of magnesian carbonates yields working curves which are equally useful for and directly applicable to analyses of several basic silicate rocks, at least for magnesia.

D. *Carbonate rocks—Limestones and Dolomites*

Carbonate rocks vary greatly in composition between the composition of dominant calcite and dolomite, and argillaceous and siliceous varieties are not uncommon. A ready and reasonably accurate spectrochemical method for determination of the major and minor constituents as well as of trace elements is desirable. This problem was recently investigated in making a trace-element study of Devonian dolomites in the vicinity of the Pine Point lead-zinc deposits in the North-West Territories by D. N. Jeffs (1955). Leininger (1950) previously described a d.c.-arc method for analysis of major constituents of limestones, using only graphite and sample, and calculating results according to the mutual standard method of Churchill and others. Good results were obtained, deviations calculated from chemical results ranging from 1·7 to 21%. Since this work was completed, Goldsmith, Graf, and Joensuu (1955) have described a spectrochemical method for the determination of major and minor constituents of such material, designed to overcome loss of carbonates on arcing due to evolution of carbon dioxide, and employing cobalt and barium as internal standards with

samples which are first fluxed with lithium carbonate and boric acid, after the method of HASLER and BARLEY (1952).

The strontium carbonate–Stallwood air-jet method described for siliceous igneous rocks was found equally useful for a wide range of carbonate rocks. In the first trial the 1 : 1 : 2 mix of sample : $SrCO_3$: graphite was used, but in order to bring up low concentrations of trace elements in the particular dolomites involved, a second method using a mixture 2 of sample to 1 $SrCO_3$ to 1 graphite was also developed. In none of our experiments was any difficulty encountered due to loss of sample on arcing.

As the accurate determination of magnesia is important in the classification of carbonate rocks, still greater precision and accuracy was sought for this oxide than was obtained with strontium carbonate. The substitution of barium carbonate for the strontium salt in the 1 : 1 : 2 mixture was found to give smoother burning qualities to such samples and to improve both reproducibility and accuracy. Furthermore, certain line pairs of Mg and Ba yield intensity-concentration curves with carbonates which practically coincide with similar curves developed for basic silicate rocks. Both methods are detailed below.

1. *Strontium carbonate methods*

Standards for major and minor constituents—For the major and minor constituents, two sets of standards were prepared by two individuals to yield mixtures of carbonates with the ranges of oxides shown in Table 10. In one set of standards (A-K) the base consists of a 1 : 1 mixture of National Bureau of Standards dolomite No. 88 and burnt refractory No. 77, to which spec-pure ferric oxide and Mn_3O_4 were added to give 1·62% Fe_2O_3 and 1·00% MnO. Aliquots of this base were then diluted with given amounts of dolomite No. 88 or pure crystalline calcite to yield the desired concentrations.

A second set (Nos. 1–9) was prepared by making various mixtures of two bases, one a 1 : 1 mix of N.B.S. dolomite No. 88 and limestone (No. 1A) and the other of plastic clay No. 98.

No attempt has been made to prepare standards with the low amounts of alkalies usually present in such rocks, as these are best determined by flame photometer methods.

Table 10. Range in composition of standards

	A–K Percentage	1–9 Percentage
CaO	15·36–52·8	23·87–35·90
MgO	2·66–20·18	8·72–12·8
Fe_2O_3	0·014–2·00	0·90– 1·25
MnO	0·003–0·50	0·015–0·022
SiO_2	0·09–27·50	7·21–24·73
Al_2O_3	0·06–18·87	3·14–10·01
TiO_2	0·006–1·18	0·08– 0·53

As check standards, several mixtures of a very pure dolomite, used as a source of magnesium at Haley, Ontario, and containing no detectable silica and only a very faint trace of aluminium, and of plastic clay No. 98, were prepared especially to test intensity-concentration curves for alumina and silica. In addition, analyses were made of N.B.S. argillaceous limestone No. 1A and dolomite No. 88 alone, to determine relative accuracy.

Standards for trace elements in carbonates—Trace-element standards have to date been prepared only in a dolomite base (No. 88 N.B.S.). These have been made by additions of spec-pure oxides of Zn, Cu, Ni, B, and In, nitrates of Pb and Ag, and sodium bismuthate for Bi. Dilutions with dolomite gave a range from 0·004% Zn and 0·0005% Pb, Cu, Ni, Ag, B, Bi, and In, up to 0·006% for Ni, Ag, Bi, 0·02% Cu, and 0·2% lead and zinc.

As noted above, these standards were run with strontium carbonate and graphite first in a 1 : 1 : 2 mix, which was later changed to 2 : 1 : 1. In both cases excellent intensity-concentration curves were obtained with close-to-unit slope.

No. 88 dolomite mixed with strontium carbonate (2 : 1 : 1) was found, however, to contain small amounts of lead and copper. These were determined by the addition method to be 0·0018% lead and 0·0014% copper, and corrections were applied to standards containing this

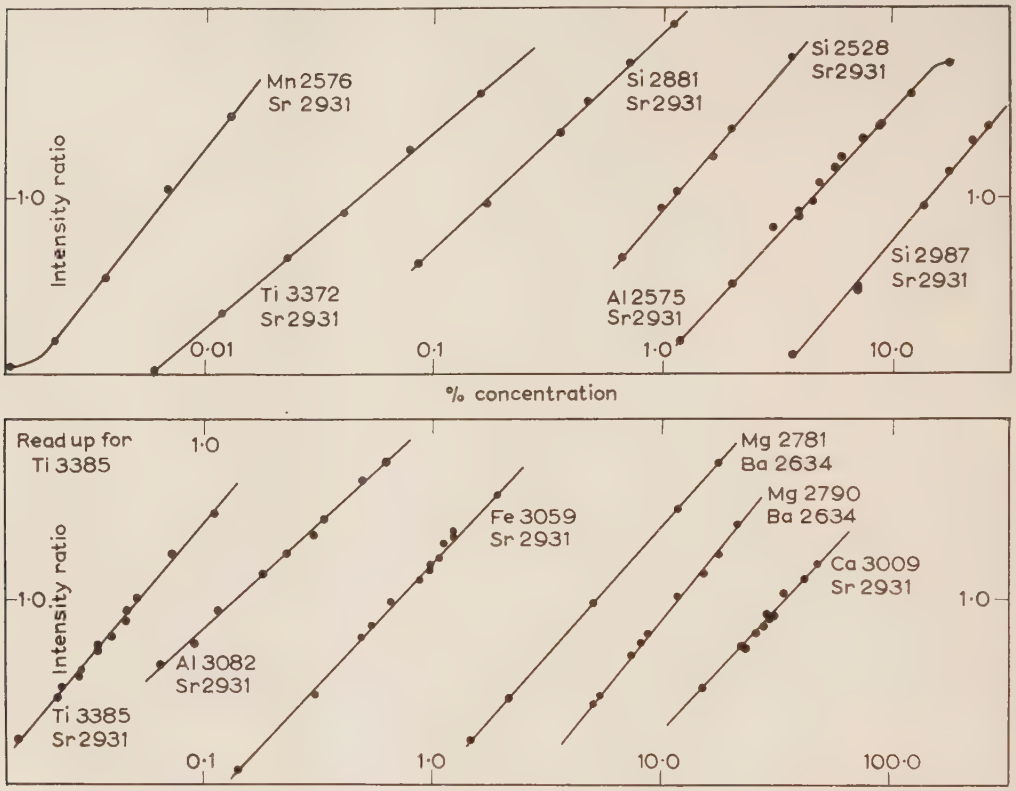

Fig. 3. Intensity ratio–concentration curves for constituents in limestones and dolomites.

base. As noted earlier under trace elements in granite, the strontium carbonate appears in the 1 : 1 : 2 mixtures to account for 10 p.p.m. Cu and a background effect of 20 p.p.m. appeared there for Pb. In the latter case therefore a minus correction is necessary to give the correct lead content of an unknown and a plus correction for copper in the 2 : 1 : 1 mix of about 9 p.p.m.

Spectrographic conditions—The following are spectrographic conditions used:

	Major and minor 1 : 1 : 2 mix	Trace elements 2 : 1 : 1
Time	60 sec	50 sec
Gap	4 mm	3 mm
Amps	4·5	9
Slit	40 μ	40 μ
Transmission	100%	80%
Grating doors	0·5	0·2
Crater electrodes	$\frac{3}{32}$ in. in $\frac{1}{8}$-in. electrode	$\frac{3}{32}$ in. in $\frac{1}{8}$-in. electrode
Film	S.A. No. 1	S.A. No. 1

Lines and ranges in composition—A great deal of study has been devoted to the selection of suitable lines for various elements, particularly for Al, Si, and Mg, and those finally selected (Table 11) for given ranges in composition yield curves of good linearity when plotted on intensity-concentration diagrams (Fig. 3).

As shown by plots of the two sets of standards and check standards, errors in these are of a relatively small order. Other lines, however, such as Si-2516·1, for some standards, give poor linearity, and for some reason Si-2528·5 for ranges below 1% SiO_2 gives a marked curve-shift with ratios higher than expected for CaO-rich MgO-poor samples. The lines selected avoid this complication.

Table 11. Lines and ranges in composition

Al-2652·5/Sr-2931·8	2·0–15·0% Al_2O_3
3082·1/Sr-2931·8	0·06–0·9% Al_2O_3
Fe-3059·1/Sr-2931·8	0·14–2·0% Fe total
Si-2881·6/Sr-2931·8	0·09–1·0% SiO_2
2528·5/Sr-2931·8	1·0–3·5% SiO_2
Mg-3332·2/Sr-3322·2	2·5–15·0% MgO
2928·8/Sr-2931·8	6·0–25·0% MgO
Ca-3009·2/Sr-2931·8	15·0–50·0% CaO
Mn-2576·1/Sr-2569·5	0·002–0·02% MnO
Ti-3372·8/Sr-2569·5	0·006–0·15% TiO_2
3385·9/Sr-2931·8	0·15–1·1% TiO_2

Lines used for traces of Ag, Cu, and Ni are the same as used for granitic rocks, but Pb-2833·3, Zn-3345·0, and Bi-3067·7 were used with Sr-2428·1 and 2569·5 for these elements.

Reproducibility

Reproducibility tests made on thirty samples of argillaceous limestone for the seven principal oxides give a relative deviation C of 3·45 to 7·8% and relative error E of 0·7 to 1·6% (Table 12).

For trace elements in carbonates, relative deviations on eight samples of one standard varied from 8 to 12%, and the relative error from 3 to 4%.

Accuracy

As no well-analysed samples of carbonates showing amounts of trace elements present are available as in the case of granite and diabase, nothing can be stated as to the absolute accuracy of the method described here.

For minor and major constituents, however, the National Bureau of Standards argillaceous limestone No. 1a serves as a check. Spectrographic and chemical results on this are given in Table 12.

In the above table it is interesting to note that the difference in SiO_2 and Al_2O_3 determined chemically and spectrographically, while of opposite sign, are both opposite in direction to the systematic error found by Fairbairn and Schairer (1952) in chemical analyses of a synthetic granite. The differences

of spectrographic from the chemical determinations accordingly cannot be explained in the same way, and are possibly due to errors in the spectrographic determinations, though their magnitude is not great. With the exception of MnO, results of which could no doubt be improved, the poorest agreement is in MgO, and again the spectrographic amount is higher than the chemical. As indicated below, the substitution of $BaCO_3$ for $SrCO_3$ for determinations of MgO is recommended.

On the whole, however, the accuracy of this rapid method of analysis may be considered as satisfactory for most geological purposes.

Table 12. Analysis of argillaceous limestone No. 1a

Oxide	Chem.	Spec.	No. anal. (n)	C^x Rel. dev. (%)	E^x Rel. error (%)	Bias	% bias
SiO_2	14·11	13·64	25	3·45	0·69	−0·47	3·3
Al_2O_3	4·16	4·32	25	4·56	0·9	+0·16	3·9
TiO_2	0·16	0·18	30	5·92	1·08	+0·02	12·5
MnO	0·038	0·06	27	6·67	1·28	+0·022	58·0
Fe_2O_3	1·63	1·64	30	7·01	1·28	+0·01	0·6
CaO	41·32	41·15	26	4·28	0·84	−0·17	0·4
MgO	2·19	2·86	25	7·80	1·56	+0·67	30·6

* C and E calculated on spectrographic results alone.

A rather interesting check on the accuracy of the prepared standards was obtained by analysing certain dolomite standards for nickel, using not the intensity-concentration curves for carbonates, but one established for nickel in granite rocks with a 1 : 1 : 2 mixture.

The results are as follows:

Table 13

	Per cent nickel in dolomite standards	Per cent nickel from granite curves
1.	0·0062	0·0059
2.	0·012	0·012
3.	0·025	0·0245

In addition to confirming the accuracy of the standards, this indicates, at least in the case of nickel, that the Stallwood air-jet minimizes any matrix effect in such different samples.

2. *Barium carbonate method for magnesia in carbonates*

The ratio of sample : $BaCO_3$: graphite is 1 : 1 : 2, and spectrographic conditions are identical with those described for basic silicates. Standards used include dolomite No. 88, limestone 1a (N.B.S.), and several mixtures of these.

Line pairs used over the given ranges of MgO are:

Mg-2781·4/Ba-2634·8	2%	17% MgO
Mg-2790·8/Ba-2634·8	5%	25% MgO
Mg-2936·5/Ba-2634·8	10%	25% MgO

Smooth-burning quality of this mixture on arcing results in a very constant density of Ba-2634·8, and this line should prove equally useful for other elements than magnesium.

Intensity ratios for the first line pair on the standards give practically perfect linearity and an intensity-concentration curve close to unit slope. A precision test on Mg in limestone 1a gives a relative deviation C on thirteen samples of 4·3%, an improvement over 7·8% obtained with strontium carbonate. This curve also passes directly through plots of intensity ratio/concentration of MgO for a chlorite schist (12·56% MgO) analysed by J. A. Maxwell.

Mg-2790·8/Ba-2634·8 also yields a good curve on standards, and similar plots of intensity ratio/concentration MgO for four samples of basic silicate rocks supplied by G. M. Friedman and analysed at the Minnesota laboratory fall surprisingly close to it. Spectrographic and chemical determinations on these are given in Table 14.

Table 14. Per cent magnesia in basic silicate rocks
Determined on barium carbonate curves for carbonates

No.	Chemical %	Spec. %	Diff.	% Diff.
2033	7·26	7·38	+0·12	1·65
1915	8·09	8·30	+0·21	2·6
2032	8·76	8·90	+0·14	1·6
1916	15·28	14·50	−0·78	5·1

These examples serve as a good check on the accuracy of the method and again indicate the lack of matrix effect with the Stallwood air-jet.

Line pair Mg-2936·5/Ba-2634·8 also gives a useful curve, though of somewhat steeper slope than the others noted.

E. *Trace Elements in Ferric Oxide Iron Ores*

The strontium carbonate–air-jet method is also applicable to the analysis of trace elements in iron ores of the ferric-oxide type containing dominantly hematite and limonite or goethite.

Standards of trace elements in iron ores

Standards were prepared from spectrographically pure oxides to simulate as closely as possible the composition of ore from Steep Rock Iron Mines, Ontario, and Mesabi, Minnesota, in content of Fe_2O_3, SiO_2, Al_2O_3, MgO, CaO, and MnO. In terms of elements or oxides, this base had the composition Fe 62·74, SiO_2 7·9, Al_2O_3 1·4, Mn 0·29, CaO 0·22, MgO 0·2. Trace elements were then added as spectrographically-pure oxides or compounds to an aliquot of the base, which was then successively diluted with the same base to yield desired ranges in composition.

Though not completely independent, two other sets of standards were prepared from a sample of Mesabi ore found to be very low or lacking in most trace elements, and from a composite sample of the Hogarth ore body (1954) from Steep Rock Lake. The Mesabi set was made by adding aliquots of the first set of standards to Mesabi ore, and further diluting this with the same ore. The second set was made by first analysing the (calcined) Hogarth ore on curves established by the first set of standards and then successively diluting aliquots with

spectrographically pure iron oxide. This set was used to determine whether standards containing a large proportion of natural, but calcined, ore would fit curves established on entirely synthetic samples. This was found to be the case for most of the trace elements with the exception of Co, Mo, and V, on which further work is in progress. Entirely independent check standards are also being prepared with two types of ore as a base.

Preparation of samples—As some of the ores studied contain appreciable quantities of goethite, determinations on these are carried out after heating to eliminate the bulk of combined water. Heating is carried out in an electrically-controlled furnace. By experiment it was found that heating some ores at 300°C for 24 h or at 600°C for 3 h gave practically the same loss of water. Other ores have been found to require the higher temperature. If the major part of the combined water is not eliminated, marked loss of sample occurs on arcing. The loss on heating is determined, and results of analyses are reported on a wet-ore basis.

Spectrographic conditions—Dried ores are mixed with strontium carbonate and buffer graphite in a 1 : 1 : 2 ratio, as for silicate rocks. Conditions used are similar to those for siliceous rocks, except for the following:—

Time	50 sec
Gap	3 mm
Slit	35 μ
Amp	6
Volt	300
Transmission	100%
Grating doors	0·3

Lines and ranges in composition—Lines of trace elements and compositional ranges used are given in Table 15. Sr-2569·5 was used as an internal standard line for all analytical lines, and working curves close to unit slope were obtained.

Precision—Relative deviations C on fifteen analyses for each of chromium, nickel, and vanadium amounted to 4·97, 4·11, and 8·22% respectively; that is, 67% of the determinations fall within plus or minus these percentages of the amount present.

Table 15. Lines and ranges in composition of trace elements in iron ores

Element	Line	Range in per cent
Cobalt	3453·5	0·002–0·04
Chromium	4254·3	0·002–0·06
	4289·7	0·010–0·10
Molybdenum*	3170·3	0·006–0·20
Nickel	3414·7	0·003–0·07
Lead	2833·0	0·015–0·30
Tin	2840·0	0·030–0·30
	3175·0	0·030–0·15
Titanium	3088·0	0·010–0·15
	3372·8	0·030–0·06
Vanadium	3185·4	0·003–0·20

* Fe interference fairly constant in iron-rich samples.

Accuracy—As no well-analysed samples were available to check the accuracy of the method, an entirely separate set of standards was prepared containing known amounts of chromium, niobium, and arsenic for analysis of these elements by means of a Philips X-ray spectrograph. These standards were prepared in the synthetic-hematite base described above. To these selenium is added as an internal standard with lithium carbonate as a diluent.

Ore samples analysed by the X-ray method are not calcined in order to avoid any loss of arsenic or other volatiles. Results of analyses of thirteen samples of ore by the optical and X-ray spectrographs are given in Table 16. For nine of the thirteen samples agreement by the two methods is good, and varies from 0·001 to 0·003% in the ore as a whole.

Table 16. Chromium analyses of iron ores (per cent chromium)

No.	Spectro-graphic	X-ray		Difference	
		1	2	Max. diff.	Min. diff.
A-6	0·050	0·051	0·052	0·002	0·001
A-7	0·014	0·015	0·017	0·003	0·001
A-8	0·044	0·039	0·034	0·010	0·005
A-9	0·030	0·030	0·027	0·003	0·000
A-10	0·022	0·021	0·022	0·001	0·000
A-11	0·006	0·011	0·012	0·006	0·005
A-12	0·005	0·007	0·007	0·002	0·002
A-13	0·010	0·010	0·011	0·001	0·000
A-14	0·019	0·025	0·024	0·005	0·005
A-15	0·022	0·024	0·023	0·002	0·001
A-16	0·049	0·047	0·047	0·002	0·001
A-17	0·010	0·012	0·011	0·002	0·001
A-19	0·012	0·016	0·016	0·004	0·004

4. Conclusions

The results of an intensive investigation of spectrographic methods utilizing the Stallwood air-jet and a d.c.-arc discharge for the analysis of major, minor, and trace-element constituents in siliceous igneous and metamorphic rocks and minerals, in basic and hydrous silicate rocks, in various carbonate rocks ranging from limestone to dolomite, and of some trace elements in ferric oxide types of iron ores, are presented.

The results indicate that analyses of suitable and in many cases of high accuracy, adequate for most geological investigations of such materials, may be obtained by these relatively rapid methods.

The use of strontium carbonate (after Kvalheim) as an internal standard is advocated for most procedures, but barium carbonate has been found more suitable for basic silicate rocks and for magnesia in carbonates. For Ba, Sr, and Pb determinations in siliceous igneous or metamorphic rocks, potassium sulphate is used instead of the carbonate.

For siliceous granitic rocks an accuracy of close to 5% or less of the chemical determinations is indicated for most of the major constituents, and an acceptable accuracy for minor constituents is shown. A close approximation of the amount

of silica in such rocks may be obtained by difference, but a rapid colorimetric check is useful. Alkalies in the low ranges, also, seem best determined or checked frequently by flame photometer methods.

Reproducibility tests on G-1 granite and W-1 diabase are given and results of chemical and spectrographic analyses of five other siliceous rocks are compared.

For siliceous rocks, a potassium sulphate method and three strontium carbonate methods, in which ratios of sample to $SrCO_3$ to graphite are varied along with discharge conditions, yield trace-element determinations on the G-1 granite and W-1 diabase which, for the most part, closely check the recommended values given by Ahrens.

Attempts to apply working curves developed for siliceous rocks to the analysis of more basic rocks have been unsuccessful, but the substitution of barium for strontium carbonate yields much better results, which are being further studied.

The application of the strontium carbonate–air-jet method to carbonate rocks for major, minor, and trace-element constituents has been reasonably successful, and yields a relative deviation of the order of 3·5 to 7·8% for seven principal oxides and of 8 to 12% for several trace elements. Increasing the amount of sample increases the sensitivity obtainable on trace elements in carbonates. Substitution of barium for strontium carbonate for the determination of magnesia yields perfectly linear working curves which may be used for analysis of basic silicate rocks for this oxide as well. Examples of analyses of basic silicates on these curves are given. Both this and the fact that carbonates may be analysed for nickel on strontium carbonate curves established for granite rocks indicate the negligible matrix effect produced with the air-jet, at least for certain elements or oxides.

Similar methods may be applied to the determination of trace elements such as Co, Cr, Mo, Ni, Sn, Ti, and V in ferric-oxide types of iron ores. Examples are given of chromium determinations made by both the optical and X-ray spectrograph. Samples ranging from 0·005 to 0·05% Cr yield results differing for the most part by 0·001 to 0·003%. Four out of thirteen show minimum differences of 0·004–0·005% in the ore.

These investigations have been inspired by the desire to further geochemical studies of a wide range in both the petrology of igneous, sedimentary, and metamorphic rocks, and economic geology. It is hoped they will bear fruit in several graduate and other researches now under way.

Acknowledgements—The research involved in this study has been made possible by grants-in-aid by the Research Council of Ontario and the Geological Survey of Canada. The kind co-operation of Dr. Maurice Haycock and Dr. W. M. Gray, Mines Branch, Ottawa, is also gratefully acknowledged. The writers are indebted to A. W. Helz and K. J. Murata for a critical reading of the manuscript.

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Some anomalous K/Rb ratios in igneous rocks and their petrological significance

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(*Received* 10 *January* 1956)

Abstract—Basalts, andesites, and trachytes from Bank's Peninsula (New Zealand), and granodiorites, felsites, and granophyres from Slieve Gullion (County Armagh), have K/Rb ratios in agreement with those of Ahrens *et al.* (1952, 1954a) for a wide range of igneous rocks and meteorites. Unaltered granites from St. Austell (Cornwall), and the Mourne Mountains (County Down), and rhyolites from Bank's Peninsula, have significantly lower ratios (i.e., enrichment in rubidium relative to potassium). It is concluded that these rocks have crystallized from an extremely differentiated magma. The abundances of Ba, Sr, and Zr lend some support to this hypothesis.

Introduction

Ahrens, Pinson, and Kearns (1952) have drawn attention to the uniformity of the K/Rb ratio, which averages 100 for meteorites and 90 for terrestrial igneous rocks. Ahrens (1954a, p. 815), after considering some fresh data, states further that "The close association of potassium and rubidium in rocks and meteorites is evident, and calculation shows that (these ratios) are equal to within about 5 per cent."

The data quoted by Ahrens *et al.* (1952) were obtained by spectrographic analysis (see Ahrens, 1954b, pp. 47–73). The granite (G-1) and diabase (W-1) were used as standards with rubidium values of 560 p.p.m. and 64 p.p.m. (Ahrens, 1954b, Table 3-3). It now appears that these values are too high. Smales (1955), using radioactivation analysis, reports average values of 239 p.p.m. Rb for G-1 and 28 p.p.m. Rb for W-1. Herzog and Pinson (1955), using the isotope dilution technique, give rubidium averages for G-1 and W-1 of 217 and 29 p.p.m. respectively. It should be noted that Ahrens (1954b, Table 3-2) reports spectrographic determinations by Nockolds of 240 p.p.m. Rb in G-1 and 20 p.p.m. Rb in W-1.

It seems likely that the true rubidium contents of G-1 and W-1 lie within the ranges 215–240 p.p.m. and 25–30 p.p.m. respectively. This does not destroy the validity of Ahrens's (1952) conclusion, but merely shifts the average ratio from 90 to about 240.

Analytical Data

Determinations were made of the alkali elements during investigations by the authors of igneous suites from Bank's Peninsula (New Zealand), St. Austell (Cornwall), and Slieve Gullion and the Mourne Mountains (Ireland). Sodium and potassium were determined by flame photometer and rubidium on a Hilger large quartz and glass spectrograph, using the variable internal-standard method described by Ahrens (1954b, pp. 52–59) (see footnote). Both sodium

Footnote—Glass optics; wavelength range 4600–9600 Å; current, 3-amp d.c.; anode excitation; samples burnt to completion of alkali metal distillation; graphite electrodes, anode 2·4 mm diameter × 5 mm deep; slit 20 microns; step sector; Kodak II-N plates developed for 5 min in Kodak D-19B developer. Lines read with a Hilger nonrecording microphotometer.

Table 1. Analytical results

		%K	p.p.m. Rb	K/Rb
	(a) Bank's Peninsula, New Zealand			
T-86	Gabbro, Onawe	0·26	9	289
T-49	Olivine basalt, Halswell	1·00	30	333
T-94	Dolerite, Cooper's Knob	1·05	43	244
T-104	Olivine basalt, Ahuriri Lagoon	0·82	20	410
T-115	Basalt, Diamond Harbour	0·92	35	263
T-83	Basalt, Duvauchelle Bay	0·68	24	283
T-100	Basalt, Duvauchelle Bay	1·44	56	257
T-111	Dolerite, French Farm	1·30	49	265
T-80	Olivine basalt, Green Point, Akaroa	0·90	33	273
T-101	Basalt, Barry's Bay Road	1·08	34	318
T-98	Basalt, Stony Bay Road	0·97	27	359
T-112	Olivine basalt, Hilltop	0·75	20	375
T-113	Olivine basalt, Okains Peak	1·05	34	309
T-124	Olivine basalt, Devil's Gap	1·28	39	328
T-56	Andesite, McQueen's Valley	2·65	110	241
T-126	Andesite, Governor's Bay	2·65	153	173
T-69	Andesite, Lyttelton	1·28	49	261
T-70	Andesite, Lyttelton	1·38	43	321
T-77	Andesite, Summit Road	1·31	39	336
T-62	Andesite, Glenmore Quarry	1·68	57	295
T-102	Andesite, Devil's Knob	2·00	53	377
T-73a	Trachyte, Lyttelton	3·25	175	186
T-73b	Trachyte, Lyttelton	3·86	140	276
T-48	Trachyte, Cass Peak	3·10	135	240
T-66	Trachyte, Evans Pass	3·06	125	245
T-106	Trachyte, Le Petit Carenage	3·90	125	312
T-107	Trachyte, Tekao Bay	3·64	140	260
T-81	Trachyte, Akaroa	4·21	130	301
T-123	Trachyte, Devils Gap	4·59	205	224
T-85	Syenite, Onawe	2·90	105	276
T-57	Rhyolite, Gebbies Pass	3·89	355	110
T-61	Rhyolite, Mansons Peninsula	3·08	365	84
T-96	Rhyolite, Gebbies Pass	3·80	345	110
	(b) St. Austell, Cornwall			
1.	Biotite-muscovite granite (An 28)	5·00	475	105
2.*	Early lithionite granite (An 7)	3·84	345	111
3.	Late lithionite granite (An 4)	3·90	800	49
4.*	Fluorite granite (An 4)	4·03	515	78
	* Average of three analyses.			
	(c) Slieve Gullion, Co. Armagh			
G-83	Hornblende biotite granodiorite 1½ m NNW Mullaghbawn	2·86	120	238
G-309	Hornblende biotite granodiorite 1 m SE Mullaghbawn	2·15	115	187
G-328	Biotite granodiorite, ¼ m SW Camlough	3·09	145	213

Table 1 (*continued*)

		%K	p.p.m. Rb	K/Rb
	Slieve Gullion, Co. Armagh (*continued*)			
G-330	Hornblende biotite granodiorite, $1\frac{1}{4}$ m WSW Camlough	3·04	135	225
G-333	Hornblende biotite granodiorite, 3 m N of Mullaghbawn	3·26	115	283
G-338	Hornblende biotite granodiorite, $1\frac{1}{2}$ m N of Mullaghbawn	2·89	140	206
G-339	Hornblende biotite granodiorite, $\frac{3}{4}$ m NW Mullaghbawn	2·84	115	247
G-106	Porphyritic Felsite, 1 m WSW Forkill	4·92	225	219
G-111	Porphyritic Felsite, $\frac{3}{4}$ m SW Forkill	3·72	170	219
G-313	Porphyritic Felsite, $1\frac{1}{2}$ m ESE Forkill	4·89	235	208
G-314	Porphyritic Felsite, $\frac{1}{2}$ m SE Forkill	4·50	215	209
G-315	Porphyritic Felsite, $\frac{2}{3}$ m NW Forkill	3·79	215	176
G-317	Porphyritic Felsite, $1\frac{1}{4}$ m NW Forkill	4·37	195	224
G-70	Porphyritic granophyre, $1\frac{1}{2}$ m NW Mullaghbawn	4·97	210	237
G-331	Porphyritic granophyre, Sturgan Mt.	4·53	225	201
G-332	Porphyritic granophyre, Sugarloaf Hill	4·34	220	197
G-335	Porphyritic granophyre, Slievenacappel	4·46	220	203
G-336	Porphyritic granophyre, $2\frac{1}{2}$ m N Mullaghbawn	4·46	240	186
G-337	Porphyritic granophyre, $2\frac{1}{2}$ m N Mullaghbawn	4·92	200	246
	(d) West Mourne Mountains, Co. Down			
M-118	Granite, G-4, 4 m NNE Rostrevor	4·03	380	106
M-120	Granite, G-5, 3 m S 8° E Hilltown	4·10	285	144

and potassium were used as internal standards. G-1 and W-1 were used as standards, values of 240 p.p.m. (G-1) and 28 p.p.m. (W-1) being used for Rb, and for Na and K the figures recommended by Ahrens (1954b, Table 3-3). Fig. 1 shows the working curves employed. The analytical results are reported in Table 1.

Geological and petrographical information for the St. Austell granite will be found in Exley (1955), and for the Mourne granites in Emeleus (1955). Papers dealing with Bank's Peninsula (S. R. T.) and Slieve Gullion (C. H. E.) will appear subsequently.

Discussion

Fig. 2 shows the close association of K and Rb. Except for those values falling in area *A*, the results fall within the limits of scatter in Fig. 1 of Ahrens *et al.* (1952, p. 240). The straight line of that diagram has been adjusted in Fig. 2 to conform to the changed rubidium values of G-1 and W-1. Ahrens's graph is based on 190 determinations of rubidium, using G-1 and W-1 as standards and the analytical method described by Ahrens (1954b, Section 5-4). In Fig. 2, the limits of scatter of points on Ahrens's diagram are indicated by the cross-bars. It will be seen from this figure that the normal K/Rb relation holds for the Bank's Peninsula basalts, andesites, and trachytes, and the Slieve Gullion granodiorites, felsites, and granophyres: but that the Bank's Peninsula rhyolites, the St. Austell

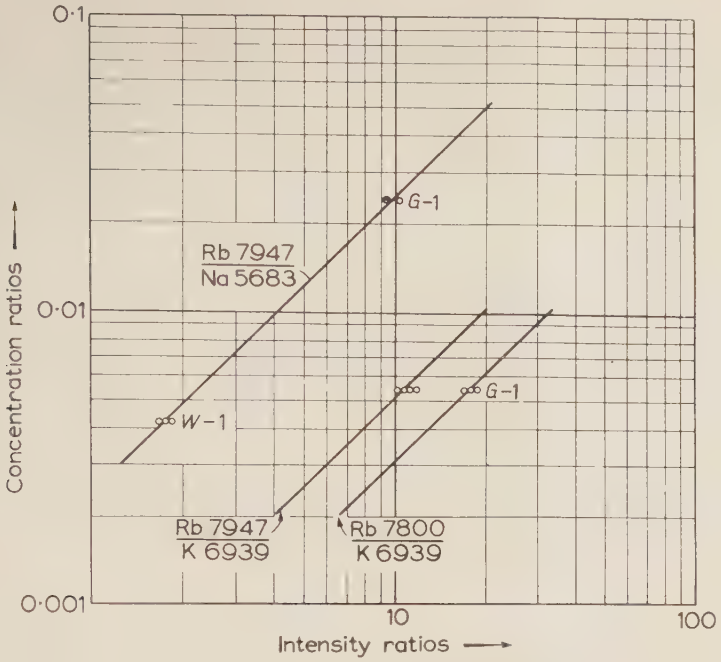

Fig. 1. Working curves used for the determination of rubidium.

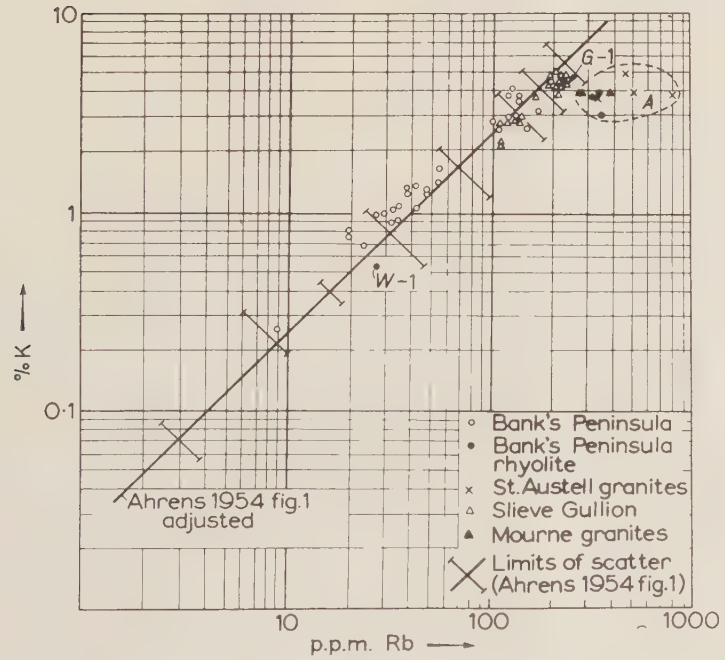

Fig. 2.

granites, and the Mourne granites (all in area *A* of Fig. 2) show relative enrichment in rubidium.

Such enrichment is a well-known feature in the crystallization products of late small-volume residual solutions, e.g., aplites, pegmatites (Rankama and Sahama, 1950, pp. 436–439; Ahrens *et al.*, 1952, p. 239; Ahrens, 1953, p. 11; Nockolds and Allen, 1953, p. 137). It is, however, an unusual feature in normal igneous rocks. It has been noted in the potassium-poor lavas of Crater Lake and the Lesser Antilles (Nockolds and Allen, 1953, p. 137). Patterson (1952, 1953) has observed general rubidium enrichment (compared with Ahrens's data) in the Tertiary lavas of N.E. Ireland and in the acid intrusives of Slieve Gullion and the Mourne Mountains. His data are, however, semiquantitative (Patterson, 1952, p. 173; 1953, p. 289) and, since G-1 and W-1 were not used as standards, are perhaps not directly comparable with data obtained using these standards. The low K/Rb ratios in the Bank's Peninsula rhyolites, Mourne and St. Austell granites, suggests that these rocks crystallized from a magma which had undergone differentiation to a degree typical of the pegmatitic phase rather than the less extreme differentiation common in normal acid igneous rocks.

Table 2

	Ba	Sr	Zr
Bank's Peninsula rhyolites	<10	<10	115
St. Austell granites	105	60	47
Mourne granites	230	45	310
Average of 42 American granites	1300	180	170

At this stage, the magma may have become impoverished in trace elements common in less highly differentiated acid rocks. In this connection it is interesting to compare (Table 2) the values for barium, strontium, and zirconium in the Bank's Peninsula rhyolites, St. Austell and Mourne granites with the arithmetical mean of forty-two determinations of these elements in North American granites, determined spectrographically using G-1 and W-1 as standards (Ahrens, personal communication). The figures for these North American rocks are quite similar in magnitude to data for other granites (e.g., Nockolds and Allen, 1953, Table 5: Scottish Caledonian granites), but have the advantage of being directly comparable with our data. With the exception of zirconium in the Mourne granite, these elements are markedly less abundant than the granite averages. Comparable effects in the Scottish Caledonian aplites were noted by Nockolds and Allen (1953, Table 5, p. 136) and in the latest rhyolites of the East Central Sierra Nevada lavas (*op. cit.*, Table 4, p. 136). For Skye granites and granophyres, Professor L. R. Wager (personal communication) has found similar depletion in Ba and Sr at the extreme acid end of the differentiation sequence.

The above evidence, in conjunction with the rubidium enrichment, leads to the hypothesis that these rocks crystallized from an extremely differentiated magma. The absence of pegmatites associated with the Mourne and St. Austell

granites may indeed indicate that no pegmatic phase separated. The geochemical data tend to support the view that the latter intrusion is not isolated, but is merely a cupola of a more extensive, presumably less highly differentiated, granite at depth. It seems worth while mentioning here that CANNEY (1952), employing a similar spectrographic technique to ours, found the K/Rb ratio in 323 sedimentary rocks to show the same uniformity as AHRENS's data (1952) for igneous rocks. Granites formed from sediments by a granitization process might thus be expected to have the usual K/Rb ratios, and it seems difficult to account for the abnormal ratios reported here by other than igneous processes.

The enrichment of rubidium in the pegmatitic phase has been ascribed by AHRENS (1953) to the 12% radius difference between K^+ (1·33 Å) and Rb^+ (1·47 Å), this behaviour certainly being in accord (at this late stage of differentiation) with the classical Goldschmidt rule.

Acknowledgements—The authors are grateful to Professor L. R. WAGER and Dr. L. H. AHRENS for their interest and advice, and to Mrs. A. BLACKBURN and Dr. M. WEIBEL for assistance with the analyses.

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Age of meteorites and the earth

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(*Received* 23 *January* 1956)

Abstract—Within experimental error, meteorites have one age as determined by three independent radiometric methods. The most accurate method (Pb^{207}/Pb^{206}) gives an age of $4{\cdot}55 \pm 0{\cdot}07 \times 10^9$ yr. Using certain assumptions which are apparently justified, one can define the isotopic evolution of lead for any meteoritic body. It is found that earth lead meets the requirements of this definition. It is therefore believed that the age for the earth is the same as for meteorites. This is the time since the earth attained its present mass.

It seems we now should admit that the age of the earth is known as accurately and with about as much confidence as the concentration of aluminium is known in the Westerly, Rhode Island granite. Good estimates of the earth's age have been known for some time. After the decay-constant of U^{235} and the isotopic compositions of common earth-leads were determined by Nier, initial calculations, such as Gerling's, roughly defined the situation. Approximately correct calculations were made by Holmes and by Houtermans on the basis of bold assumptions concerning the genesis of lead ores. Subsequent criticism of these calculations created an air of doubt about anything concerning common leads and obscured the indispensable contributions which these investigators made in establishing the new science of the geochemistry of lead isotopes. When the isotopic composition of lead from an iron meteorite was determined, we were able to show that a much more accurate calculation of the earth's age could be made, but it still was impossible to defend the computation. Now, we know the isotopic compositions of leads from some stone meteorites and we can make an explicit and logical argument for the computation which is valid and persuasive.

The most accurate age of meteorites is determined by first assuming that meteorites represent an array of uranium-lead systems with certain properties, and by then computing the age of this array from the observed lead pattern. The most accurate age of the earth is obtained by demonstrating that the earth's uranium-lead system belongs to the array of meteoritic uranium-lead systems.*

The following assumptions are made concerning meteorites: they were formed at the same time; they existed as isolated and closed systems; they originally contained lead of the same isotopic composition; they contain uranium which has

* C. Patterson: N.R.C. Conference on nuclear processes in geologic settings, 1955 September meeting, Pennsylvania State University. Except for minor disagreements, this paper is probably a concrete expression of the attitudes of most investigators in this field, both here and in Europe. The author is grateful to his colleagues, Clayton, Inghram, Tilton, Wasserburg, and Wetherill, for their criticisms which helped clarify this paper.

the same isotopic composition as that in the earth. On the basis of these assumptions various leads might be expected to evolve as a result of different original U/Pb ratios in separate meteorites, and an expression* for any pair of leads derived from such an array is:

$$\frac{R_{1a} - R_{1b}}{R_{2a} - R_{2b}} = \frac{(e^{\lambda_1 T} - 1)}{k(e^{\lambda_2 T} - 1)} \qquad (1)$$

where $R_1 = Pb^{207}/Pb^{204}$ and $R_2 = Pb^{206}/Pb^{204}$ for leads from different meteorites a and b, $k = U^{238}/U^{235}$ today (137·8), $\lambda_1 = U^{235}$ decay-constant ($9{\cdot}72 \times 10^{-10}$ yr^{-1}), $\lambda_2 = U^{238}$ decay-constant ($1{\cdot}537 \times 10^{-10}$ yr^{-1}), and T = age of the array.

The isotopic compositions of leads isolated from three stone and two iron meteorites are listed in Table 1 (Patterson, 1955). Because the radiogenic and nonradiogenic leads may occur in different mineral environments in a stone meteorite and the sample dissolution procedures may be chemically selective, the lead ratios for the first three meteorites in Table 1 have estimated errors from the absolute of about 2%. The lead ratios for the last two meteorites in Table 1 have estimated errors from the absolute of about 1%.

Table 1. The isotopic compositions of lead in meteorites

Meteorite	Pb Composition		
	206/204	207/204	208/204
Nuevo Laredo, Mexico	50·28	34·86	67·97
Forest City, Iowa	19·27	15·95	39·05
Modoc, Kansas	19·48	15·76	38·21
Henbury, Australia	9·55	10·38	29·54
Canyon Diablo, Arizona	9·46	10·34	29·44

These leads cover an extreme range in isotopic composition and satisfy expression (1), yielding, within experimental error, a unique value of T. This is illustrated in Fig. 1, where it is shown that the Pb^{206}/Pb^{204} and Pb^{207}/Pb^{204} ratios from meteorite leads lie on a straight line whose slope corresponds to an age of $4{\cdot}55 \times 10^9$ yr. The dotted lines indicate how stone meteorite leads have evolved. It is clear that the assumptions of the age method are justified by the data. Errors in the lead data and in the decay-constants contribute about equally to the overall error in the calculated age, which amounts to about $1\frac{1}{2}$%. The age for the meteorite array is calculated to be $4{\cdot}55 \pm 0{\cdot}07 \times 10^9$ yr.

The assumptions have not been shown to be unique. The data can be explained

* A similar form of this expression was first used by A. Nier in 1939. F. Houtermans has termed the expression an "isochron." References for the constants are: (k) M. Inghram; Vol. 14 Manhattan Project Tech. Sev., Div. 2, Gaseous Diffusion Project, Chap. V, p. 35 (1946); (λ_1, λ_2) E. Fleming, A. Ghiorso, and B. Cunningham: *Phys. Rev.* **88**, 642 (1952).

by other qualifying or even contradictory assumptions. Most of these can be excluded as improbable. One common criticism should be mentioned: the time of a process of division or agglomeration of meteoritic material (without differentiation) cannot be distinguished by this age method. It seems probable that any such process of division or agglomeration would be accompanied by chemical differentiation. Any meteorite which had a differentiation history after its initial formation would fall off the isochron. The five meteorites in Table 1 represent a most extreme range of differentiation which occurred during the initial process of

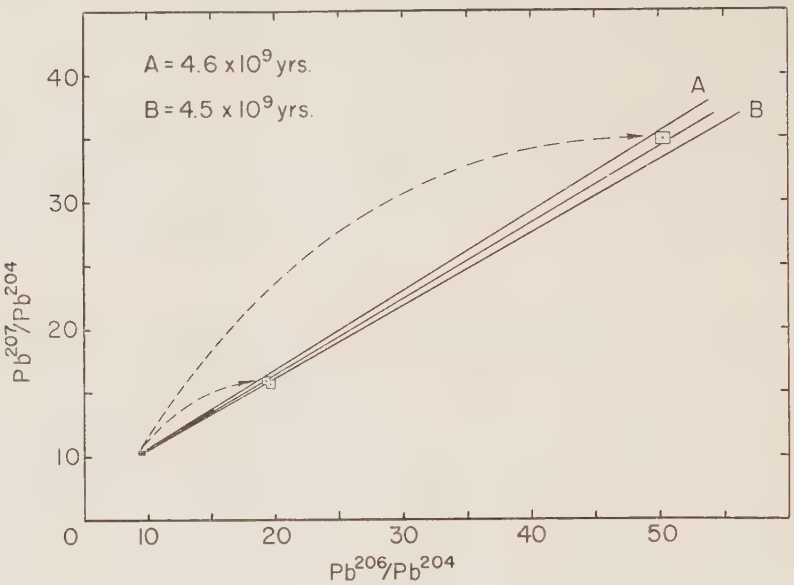

Fig. 1. The lead isochron for meteorites and its estimated limits. The outline around each point indicates measurement error.

formation. This criticism is not serious as far as meteorites are concerned, since if it were valid the lead-lead isochron would date the occurrence of differentiation processes; however, it is important with respect to the age of the earth and will be mentioned later.

At the present time, the next most accurate meteorite age is determined by the A^{40}/K^{40} method. The argon ages of six stone meteorites, three of them determined by WASSERBURG and HAYDEN (1955), and three of them determined by THOMSON and MAYNE (1955), are listed in Table 2. The age of *Forest City* has been redetermined without change by REYNOLDS and LIPSON (1955). Two sets of ages are calculated on the basis of the two reasonable limits of the e^-/β^- branching ratio.

The 0·085 branching ratio is the value obtained by studies of old potassium minerals dated by uranium-lead techniques. The 0·125 branching ratio is the value obtained by counting techniques and by direct measurements of the amounts of decay products. The difference between the two values can be accounted for by systematic loss of radiogenic argon in the old potassium minerals. If one assumes

that a fixed amount of about 20% of radiogenic argon is lost from all stone meteorites, i.e. using a branching ratio of about 0·10, then there is agreement of lead and argon ages for the same stone and an indication that the stones have existed as cold and solid bodies since they were formed. Argon meteorite ages different from the ones mentioned here have been reported by GERLING (1951), and PAVLOVA GERLING and RIK (1954). Since errors in the data presented by GERLING and PAVLOVA cannot be evaluated with any certainty, we cannot be concerned by differences between ages calculated by them and ages calculated from other data. Because of logarithmic behaviour, values for calculated ages of these old samples are insensitive to changes in the e^-/β^- branching ratio. For this reason only disagreements of about 15% between A^{40}/K^{40} and Pb^{207}/Pb^{206} meteoritic ages can be accounted for by a twofold change in the branching ratio. Large age differences must therefore be reconciled on the basis of other experimental errors. Measurements of the amounts of nonradiogenic argon in radiogenic and nonradiogenic argon mixtures are subject to large uncertainties, and for the first four meteorites in

Table 2. A^{40}/K^{40} ages of meteorites

Meteorite	Age × 10^{-9}		Investigators
	($e^-/\beta^- = 0{\cdot}085$)	($e^-/\beta^- = 0{\cdot}125$)	
Beardsley, Kansas	4·8	4·2	WASSERBURG and HAYDEN
Holbrook, Arizona	4·8	4·2	WASSERBURG and HAYDEN
Forest City, Iowa	4·7	4·1	WASSERBURG and HAYDEN REYNOLDS and LIPSON
Akabu, Transjordan	4·4	3·8	THOMSON and MAYNE
Brenham Township, Kansas	4	3	THOMPSON and MAYNE
Monze, Northern Rhodesia	2	2	THOMSON and MAYNE

Table 2, nonradiogenic argon corrections were small. For the last two meteorites in Table 2, nonradiogenic argon corrections were extremely large and the errors in calculated age are excessive. The isotope dilution determination of potassium, used by WASSERBURG and HAYDEN, is nearly an absolute method, while the flame-photometric determination of potassium, used by THOMSON and MAYNE, requires a natural absolute standard which they did not use.

The age of meteorites has been determined by the Sr^{87}/Rb^{87} method. The concentrations of rubidium and strontium and the isotopic compositions of strontium have been determined in two stone meteorites by SCHUMACHER (1955). The Rb/Sr ratio in one stone was so low that any change in isotopic composition of strontium due to radioactivity would be within experimental error. The Rb/Sr ratio in the other stone (Forest City, Iowa) was considerably higher and sufficient

to cause a 10% difference in the relative abundance of Sr^{87} when the isotopic compositions of strontium from both stones were compared.

The value for the decay-constant of Rb^{87} is in question at the present time. Reported values range from 4·3 to 6·7 $\times$ 10^{10} yr for the half-life. Part of the difficulty in the counting techniques of measuring the half-life arises from the fact that the frequency of β^-s at the low end of the energy spectrum increases rapidly with no appearance of a maximum. Measurements of decay products in terrestrial rubidium minerals dated by uranium-lead technique involve errors of open chemical systems. Schumacher's experiment probably constitutes an ideal case of the geological measurement of the half-life of Rb^{87}, since the ages have been determined by lead methods and the possibility of open chemical systems are remote. His methods of measurement are at least as accurate as the radiometric methods. One would therefore use his data to calculate the half-life of Rb^{87}, using the Pb-Ph isochron age of meteorites. The half-life of Rb^{87}, as determined by these data, is 5·1 $\times$ 10^{10} yr, and is probably the most reliable value at present. The half-life determined by the geological method on terrestrial minerals (5·0 $\times$ 10^{10} yr) agrees well with this.*

Because of the overwhelming abundance of nonradiogenic helium in iron meteorites and the large errors associated with the determination of the concentrations of uranium and thorium in iron and stone meteorites, the age of meteorites by the helium method is not accurate to much better than an order of magnitude (Paneth *et al.*, 1953; Dalton *et al.*, 1953). It has been reported that iron meteorites and the metal phases of stone meteorites were outgassed of helium as of about 5 $\times$ 10^8 yr ago, while the silicate phases of stone meteorites were not (Reasbeck and Mayne, 1955). Such an event would be highly significant and would require detailed evolutionary theory for meteorites. Recent neutron activation (Reed and Turkevich) and nuclear emulsion (Picciotto) analyses of iron meteorites show that the concentrations of uranium in these bodies are very low, and that the uranium concentrations used for helium age calculations of iron meteorites may be erroneously high. The question is unresolved at present, but it seems reasonable to believe that investigations of meteoritic helium will become vitally important to cosmic-ray studies and may be decisive in meteorite evolution theory, but cannot be used for accurate meteorite-age calculations at the present time.

The Canyon Diablo lead listed in Table 1 was isolated from troilite where the U^{238}/Pb^{204} ratio was shown by direct analysis to be 0·025 (Patterson *et al.*, 1953). This ratio is accurate to at least an order of magnitude, and it is so small that no observable change in the isotopic composition of lead could have resulted from radioactive decay after the meteorite was formed. Since stone meteorites were cold and solid during their lifetime, it is unlikely that lead transport could have occurred between iron and stone meteoritic phases if they existed in one body. This iron-meteorite lead is therefore primordial and represents the isotopic composition of primordial lead at the time meteorites were formed. Using the isotopic composition of primordial lead and the age of meteorites, expressions can be

* A value recommended by the work of the geochronology laboratory at the Dept. of Terrestrial Magnetism, Carnegie Institute of Washington.

written for a representative lead which is derived today from any system belonging to the meteoritic array:

$$Pb^{206}/Pb^{204} = 9{\cdot}50 + 1{\cdot}014\ U^{238}/Pb^{204} \quad (2)$$

$$Pb^{207}/Pb^{204} = 10{\cdot}36 + 0{\cdot}601\ U^{238}/Pb^{204} \quad (3)$$

If any two of the three ratios above can be independently measured in the earth's uranium-lead system, and they satisfy expressions (2) and (3), then this system belongs to the meteoritic array and must have its age. Two of the ratios can be measured in a sample of earth lead, but the problem of choosing such a sample is complex because the ratio of uranium to lead varies widely in different rocks and minerals whose ages are short compared to the age of the earth.

One approach is to partition the earth's crust into separate chemical systems of uranium and lead and consider their interactions. Such systems may range from minerals to geochemical cycles. Nearly all of the lead-isotope data concerns either minerals in which the uranium-to-lead ratio is very high (uraninites, etc.) or minerals in which this ratio is essentially zero (galenas). The approximate times of formation of some galenas have been determined, and of these, two dozen or so lately formed galenas may be used as a measure of earth lead (*Nuclear Geology* (1954), W. Faul, Ed.). The isotopic compositions of lead in some recent oceanic sediments have also been determined (Patterson, Goldberg, and Inghram 1953), and these may be used as a measure of earth lead.

Any of these samples will be improper or biased if they are derived from a system of uranium and lead which is only partially closed and is subject to slow but appreciable transport from other systems with different U^{238}/Pb^{204} ratios. In this respect, the sample which may represent the system of largest mass is probably the more reliable. One sample of oceanic sediment lead probably represents more material than a dozen galenas. The isotopic composition of this sediment lead is $Pb^{206}/Pb^{204} = 19{\cdot}0$ and $Pb^{207}/Pb^{204} = 15{\cdot}8$, which satisfies expressions (2) and (3) surprisingly well. It is doubtful if these figures are grossly biased, since a few measurements of uranium and the isotopes of lead in rocks with widely different U^{238}/Pb^{204} ratios indicate rather good mixing to be the first-order effect on the isotopic composition of lead in the earth's crust (Patterson, Tilton, and Inghram, 1955).

Independent of the absolute abundances of lead isotopes, a rough measure of the rates of change of the lead-isotope abundances in the earth's crust may be obtained from the isotopic composition of galenas of different ages. These rates of change are defined by the ratios of uranium and thorium to lead in the material from which the galenas are derived. From the observed rate of change of Pb^{206}, the U^{238}/Pb^{204} ratio in the earth's crust is found to be 10 (Collins, Russell, and Farquhar, 1953). This value satisfies expression (2) and (3) for sedimentary lead with unexpectedly good agreement.

In Fig. 2 it is shown that oceanic sediment lead (open circle) falls on the meteoritic lead isochron. Most of the lately formed galenas fall within the dotted outline, although a few are widely aberrant. The position of a lead along the isochron is determined by the U^{238}/Pb^{204} ratio in the system from which the lead

evolves. The arrow indicates the position on the isochron which sediment lead should occupy as predicted by the isotopic evolution of dated ore leads. Independently measured values for all three ratios adequately satisfy expressions (2) and (3), and therefore the time since the earth attained its present mass is $4{\cdot}55 \pm 0{\cdot}07 \times 10^9$ yr.

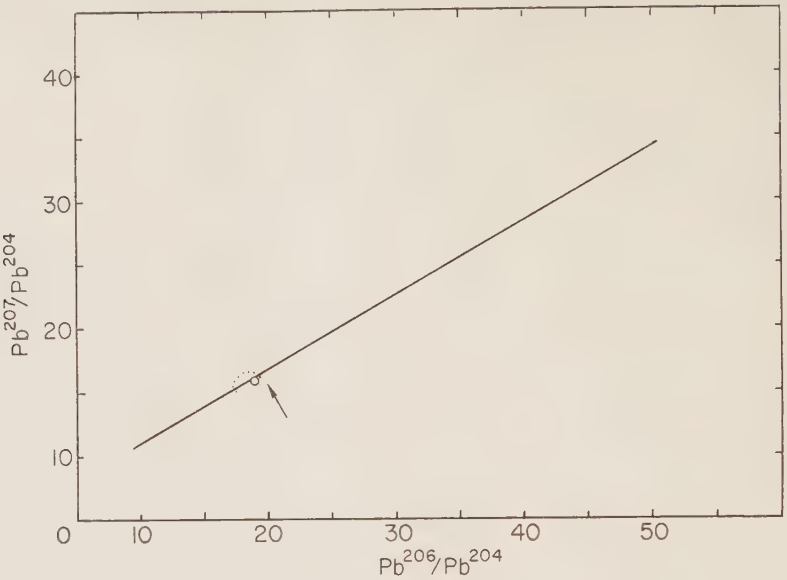

Fig. 2. The relationship between common earth leads and the meteoritic lead isochron.

If the earth is a late agglomeration without differentiation of meteoritic material then it can have any age less than meteoritic material. Rather than arguing that such a process would be accompanied by chemical differentiation (and a change of the U/Pb ratio), it seems reasonable to believe instead that such a late agglomeration process would be less probable than one where both meteorites and the earth were formed at the same time. It is a fact that extreme chemical differentiation occurred during the process which led to the mechanical isolation of the mass of material of which the earth is made, and since changes in this mass were accompanied by chemical differentiation, the Pb/Pb meteorite isochron age properly refers to the time since the earth attained its present mass.

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GEOCHEMICAL NOTE

Determinations of radiogenic Sr^{87} and Rb^{87} of an interlaboratory series of lepidolites

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(*Received* 2 *July* 1956)

Abstract—Ratios radiogenic Sr^{87}/Rb^{87} have been determined for five lepidolites ranging in age from 100 to 2700 m.y. The data agree with those obtained several years ago in this laboratory and demonstrate the reproducibility of the method of isotope dilution and the applicability of the Rb^{87} decay to mineral age measurements on lepidolites over the whole extent of geologic time.

A SUITE of lepidolites ranging in age from 100 to 2700 m.y. have been distributed under the direction of L. H. AHRENS in an effort to obtain comparisons of analyses of these minerals for radiogenic Sr^{87} and Rb^{87} using different techniques. These samples have been analysed at the Carnegie Institution using the method of isotope dilution. The analytical procedures will be published in detail elsewhere (ALDRICH *et al.*; *J. Geophys. Res.*, in press). The minerals were analysed as received.

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Table 1. Analytical data inter

Sample No.	Location	Weight sample (mg)	Rb^{87}/Rb^{85} Sample and Tracer	mg Rb sample
N 45	Bikita Quarry, S. Rhodesia	40·2 ± 0·2	0·650 ± 0·004	1·329 ± 0·02
A 106	Bob Ingersoll Mine, Keystone, S. Dak.	60·1 ± 0·2	0·628 ± 0·003	0·725 ± 0·007
		57·2 ± 0·2	0·741 ± 0·0003	0·701 ± 0·007
		50·1 ± 0·2	0·814 ± 0·003	0·579 ± 0·006
A 107	Pala, California	136·8 ± 0·2	0·679 ± 0·002	2·41 ± 0·02
A 109	Silverleaf Mine, S. E. Manitoba	56·1 ± 0·2	0·669 ± 0·002	1·237 ± 0·01
A 110	Varuträsk, Sweden	103·0 ± 0·2	0·554 ± 0·003	2·11 ± 0·04
		30·6 ± 0·2	0·858 ± 0·004	0·628 ± 0·006

Table 1 gives the data from the analyses of these micas. The measured ratio, Rb^{87}/Rb^{85}, of the tracer plus the sample is given to show the difference between this ratio and that for normal rubidium which is 0·386. The error in the determination of rubidium becomes much larger than that in the ratio, Rb^{87}/Rb^{85}, of sample plus tracer when these two ratios are close together. The column, Sr^{87}/total Sr, gives a measure of the amount of contamination which for all of these runs is less than 0·5 μg. In no case does the correction for common Sr^{87} exceed 2 per cent. Finally, the values in the column, radiogenic Sr^{87}/Rb^{87}, are independent of the error in weighing the sample since the Rb^{87} and Sr^{84} tracers were added to the same solution in each case. The ratio in this column is required to determine the age. The Varuträsk mica was analysed using two different weighed portions of one small piece of the sample supplied. Different amounts of different preparations of Rb^{87} tracer and different amounts of Sr^{84} tracer were used in the two analyses which were performed some five months apart by different analysts.

The analyses of lepidolites from four of these pegmatites have been published (Davis and Aldrich, 1953). The radiogenic Sr^{87} content of the minerals in that study has since been found to have been erroneously tabulated (Davis and Aldrich (1956)). Table 2 presents a comparison of the analyses in the present study with those made on minerals from the same pegmatite in the earlier work. The ratios Sr^{87}/Rb^{87} vary on the average by less than 5 per cent. The greatest difference between the two sets of runs in this ratio is no larger than that previously (Aldrich *et al.*; *J. Geophys. Res.*, in press; Wetherill *et al.*; *Geochim. et Cosmochim. Acta*, in press) found for Rb minerals from the same pegmatite. The ages in table 2 are calculated from a Rb^{87} half-life of 5×10^{10} years. This value has been derived from measurements of ratios, radiogenic Sr^{87}/Rb^{87}, from micas and feldspars obtained from well-dated pegmatites (Wetherill *et al.*; Aldrich *et al.*; *Phys. Rev.*, in press).

national series lepidolites

mg Rb^{87} sample	mg Rb g sample	μg Radiog. Sr^{87} sample	Radiog. Sr^{87}/Total Sr sample	μg Sr (Radiog.) g sample	Radiog. Sr^{87}/Rb^{87}
0·376 ± 0·004	33·1 ± 0·3	14·3 ± 0·2	0·965	356 ± 5	0·0380 ± 0·001
0·205 ± 0·002	12·1 ± 0·2	5·09 ± 0·1	0·938	84·7 ± 2	0·0248 ± 0·0007
0·198 ± 0·002	12·3 ± 0·2	4·67 ± 0·1	0·903	81·6 ± 2	0·0236 ± 0·0007
0·164 ± 0·002	11·6 ± 0·2	3·80 ± 0·07	0·968	75·8 ± 2	0·0232 ± 0·0007
0·682 ± 0·007	17·6 ± 0·2	1·01 ± 0·02	0·759	7·38 ± 0·1	0·00148 ± 0·00005
0·350 ± 0·200	22·0 ± 0·2	13·3 ± 0·2	0·962	236 ± 5	0·0380 ± 0·001
0·598 ± 0·01	20·5 ± 0·4	14·8 ± 0·2	0·972	144 ± 2	0·0251 ± 0·0007
0·178 ± 0·002	20·5 ± 0·2	2·40 ± 0·08	0·944	144 ± 2	0·0251 ± 0·0007

Table 2.

Location	Date of Analysis	Sample No.	mg Rb^{87}/g sample	μg Sr^{87}/g sample	Sr^{87}/Rb^{87}	Age in m.y.
Bikita Quarry	1955	(N 45)	9·35	356	0·0381	
	1952		8·75	330	0·0377	2640
Silverleaf Mine	1955	(A 109)	6·24	236	0·0378	
	1952		7·15	272	0·0380	2640
Ingersoll Mine	1956	(A 106)	3·28	75·8	0·0232	
	1956	(A 106)	3·48	81·6	0·0236	1690
	1955	(A 106)	3·41	84·7	0·0248	
	1952		3·38	73·3	0·0217	1550
Pala, Calif.	1955	(A 107)	4·98	7·38	0·00148	106
	1952		4·12	6·50	0·00158	114

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LETTER TO THE EDITORS

On the state of our knowledge of trace elements in the ocean

(*Received* 10 *May* 1956)

THE concentrations of trace elements in the ocean are of considerable geochemical and biochemical significance. Workers in these fields have had recourse to published lists (for example, WATTENBERG, 1938, 1943; SVERDRUP *et al*,. 1942; HARVEY, 1945, 1955; RANKAMA and SAHAMA, 1950; MASON, 1952; and others) which sometimes tacitly imply that the reported concentrations are somehow representative of the whole ocean, either as averages or as typical concentration ranges. The purpose of this note is to suggest that such may be far from the case, and that most of the numbers shown in these tables cannot, even in the vaguest sense, be assumed to be representative of the oceans. Indeed it is readily conceivable that they miss the mark by orders of magnitude.

As examples of this point one might use the concentrations of the thirteen trace elements considered by KRAUSKOPF (1956) in his studies of factors determining their concentrations in the ocean. These concentrations, their original sources, and the number of samples analysed are shown in Table 1.

The concentrations of Ag, Bi, Cu, Zn, Co, and Ni from NODDACK and NODDACK (1940) are apparently based on the analysis of a single sample of surface water from the Gullmarfjord, Sweden. HABER's (1927) many determinations of silver must all be questioned on the same basis that his gold determinations must be questioned, namely, that he failed to take into account the adsorption of these metals on the glass of the sample containers. BLACK and MITCHELL (1952) analysed three samples (Mo, Ni, V, and Cr in KRAUSKOPF's table). One was from 20 metres depth 20 miles off Plymouth, England, and the other two were inshore surface samples. ERNST and HOERMANN (1936) (Mo, Ni, and V) analysed five samples from Heligoland and two North Atlantic samples, one from the Baltic current on the west central Norwegian coast; the sampling depths are not reported. (Ni was not determined on the two Atlantic samples, and Mo was not determined on one of the Heligoland samples.) The concentrations of Cd are the range of five samples of surface water from the Irish Sea (MULLIN and RILEY, 1954). BOURY (1938) analysed three surface samples from French coastal waters for Pb. STOCK and CUCUEL (1934) report on the analysis of Hg in water from Heligoland which appears to be a single sample of surface water. ISHIBASHI's (1953) W figures are from a single sample taken offshore off Sirahama, Wakayama Prefecture, Japan; two samples from the same location were analysed for Cr and two samples from 31° N latitude, 135° W longitude were analysed for V.

As for copper, RILEY (1937) reports on a series of about twenty surface samples taken along the coast of the Gulf of Mexico near the mouth of the Mississippi River. ATKINS (1932) reported on the analysis of a single sample of surface water from a standard station of the Marine Biological Association (Plymouth, England). Even the ten samples reported from the subtropical North Atlantic by KALLE and WATTENBERG (1938) are from the surface; others taken at depth gave larger concentrations, but these were suspected of contamination from the water sampler.

A fairly thorough search of the literature indicates that there have been no valid analyses of deep water samples for Sb, Ba, Cd, Cs, Ce, Cr, Co, Ga, Ge, La, Pb, Hg, Mo, Ni, Sc, Se, Ag, Tl, Th, W, Sn, V, Y, and Zr, all of which are included in one or more of the cited tables. Moreover, the reported concentrations depend on not over a dozen analyses of surface or near surface samples. Critical examination of the analytical methods used by the various investigators might indicate that some of these data are not reliable, and that some of the subsurface analyses, notably that of Au, would have to be thrown out.

There is no doubt that marine organisms concentrate trace elements, impoverishing the ambient sea water. Surface concentrations of the nutrient salts are usually only a fraction of their concentrations at greater depths, which would more nearly represent the bulk of the ocean. For example, inorganic phosphate concentrations in the surface water of the Sargasso Sea are

Table 1. Determinations of the thirteen trace elements appearing in Krauskopf's (1956) Table 1.

Element	Concentration shown by Krauskopf (p.p.m.)	Original reports of the analyses	Deep-water samples included	Number of samples analysed
Ag	0·00015–0·003	Haber (1927)	Yes	Many
		Noddack and Noddack (1940)	No	One
Bi	0·0002	Noddack and Noddack (1940)	No	One
Mo	0·0003–0·0007	Ernst and Hoermann (1936)	?	Six
	(0·012–0·016)	Black and Mitchell (1952)	No	Three
Cd	0·000032–0·000075	Mullin and Riley (1954)	No	Five
Pb	0·003–0·008	Boury (1938)	No	Three
Hg	0·00003	Stock and Cucuel (1934)	No	One?
Cu	0·001–0·015	Atkins (1932)	No	One
		Riley (1937)	No	ca. 20
		Noddack and Noddack (1940)	No	One
		Kalle and Wattenberg (1938)	No	Ten
Zn	0·005–0·021	Noddack and Noddack (1940)	No	One
W	0·00009–0·0001	Ishibashi (1953)	No	One
Co	0·0001	Noddack and Noddack (1940)	No	One
Ni	0·0001–0·0005	Ernst and Hoermann (1936)	?	Five
		Noddack and Noddack (1940)	No	One
	(0·0015–0·006)	Black and Mitchell (1952)	No	Three
V	0·0003	Ernst and Hoermann (1936)	?	Seven
	(0·0024–0·007)	Black and Mitchell (1952)	No	Three
Cr	0·00004–0·00007	Ishibashi (1953)	No	Two
	(0·001–0·0025)	Black and Mitchell (1952)	No	Three

less than a few hundredths of a microgram atom per litre (0·01 microgram atom per litre of phosphorus is 0·0003 p.p.m.), but at greater depths the concentration is as much as 200 times this figure. Even greater discrepancies are found between surface and deep silicate concentrations, and nitrate concentrations follow the same rule. Harvey (1955) has listed several mechanisms by which trace elements are concentrated by organisms, and Noddack and Noddack (1940) list factors ranging between 300 and 280,000 by which various trace metals were more concentrated in marine organisms than in the surrounding water. Carritt and Goodgal (1955) and Krauskopf have demonstrated the importance of sorption phenomena in removing ions from free solution. The abundance of particulate matter in the upper layers

(see, for example, JERLOV, 1953) could easily result in the removal of practically all the trace ions from surface waters, so that differences between filtered and unfiltered water may be large. Settling of particulate matter must effectively remove large fractions of these elements from the surface layers, to be returned to solution in deeper layers or to eventually be incorporated in the bottom sediments. It is most certainly conservative to state that there may be very little relationship between surface and deep-water concentrations of the trace elements. Yet, nearly all of the very few determinations of the trace elements to date have been made on surface samples, and their concentrations in deep water remain almost wholly unknown.

Probably too much emphasis has been placed on the uniformity of the composition of sea water, which has led to the assumptiom that a limited number of analyses suffices to characterize sea water in general. There is a constancy in the ratios of the major constituents (Na^+, Mg^{2+}, Ca^{2+}, K^+, Sr^+, Cl^-, SO_4^{2-}, Br^-, H_3BO_3, and HCO_3^- plus CO_3^{2-}) to one another, but it certainly does not extend to the nutrients and trace elements.

This note is not intended to be critical of KRAUSKOPF'S work. Criticism, if any, is due to oceanographers who have permitted the perpetuation of the notion that the concentrations of the trace elements in the sea are reasonably well-known. They are not.

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Contribution No. 840 from the
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Book reviews

HENRI and GENEVIÈVE TERMIER: **L'Evolution de la Lithosophere. I: Pétrogénèse.** 653 pp., 40 figures, 54 tables. Masson et Cie., 1956. Price Fr. 8.000 Broché, Fr. 8.800 Cartonné.

THIS is the second in a series of four volumes together making a *Comprehensive Treatise of Geology*. By 1956 progress is as follows: *Vol.* 1 (1952) *Histoire Géologique de la Biosphère; Vol.* 2 (1956) *L'Evolution de la Lithosphère I: Pétrogénèse; Vol.* 3 (in press): *Orogénèse; Vol.* 4 (in preparation): *Glyptogénèse.*

The design and ambition of the authors are to explain genesis and evolution by interpretative studies of geological phenomena.

It is generally recognized that the matter in the lithosphere, representing an assemblage of ions, is governed by the laws of physics and chemistry; but these laws must be associated with the observable objects of geology and with the new data of geochemistry and cosmochemistry.

The first part, comprising 200 pages is concerned with generalities:

(1) Constitution of matter, (2) Cosmochemistry, (3) Birth of the earth, (4) Energy in the lithosphere, (5) Building blocks of the lithosphere, (6) Material transport, (7) The minerals of the rocks, (8) Geochemistry, (9) The witnesses of time.

The second part presents the great problems of petrogenesis among which we find Magmas, The Domain of the Instable, Volcanism, Sial, Plutons and Granites, Sialic Volcanism in Orogenic Zones, Convergent and Aberrant Rocks.

In these chapters emphasis is placed on the importance of the atomic structures of minerals, the rôle of gravity as an active force in the lithosphere, the constructive action of metasomatism, and the part played by regional metamorphism in the formation and mise en place of granite through a series of migmatite, gneissic granite, anatexe granite, circumscribed granite, diapirites and intrusive granite. The great geochemical cycle is described and the interrelations between eruptive, sedimentary, and metamorphic rocks are stressed. The authors think it is highly probable that juvenile emanations ascending from below (from sima) become fixed in the upper layers of the crust of the earth and aid a progressive differentiation of sial at the cost of sima.

As shown by the authors (1952) the relations of the lithosphere with hydrosphere and biosphere are manifest. Equally important connections are now pronounced to exist between the deep layers of the earth (sima) and the base of the lithosphere.

A short and factual account cannot give justice to a work of inspiration, nor is it fair to condense more than 600 pages in a brief review. I feel that the geologist loving his subject will find great pleasure and stimulation from this book, and will eagerly await the forthcoming of the additional volumes.

TOM. F. W. BARTH

E. WM. HEINRICH: **Microscopic Petrography.** McGraw-Hill Book Company, Inc., New York, 1956. 296 pp., 70 illustrations. Price $6.50.

THE raison d'être of the present book is explained in the preface: petrography today stands as a petrological tool and no longer as an end itself; thus recent books, being preoccupied mainly with petrogenesis, have forced students to refer to older books for petrographic information. Yet many new petrographic data and many fine petrographic studies have supplemented or revised older petrographic descriptions. This new information has been used in the present book.

The methods of microscopic study are first explained. Then follow the rocks: as usual they are divided into igneous, sedimentary, and metamorphic, each division is again divided into a general and a descriptive chapter. The general chapters are brief and try to give a rapid survey of genesis, classification, texture and microstructure. The descriptions are comprehensive, well illustrated and give excellent information about the microscopic petrography of a great number of rock types. However, the enormous masses of gneisses, gneissgranites and migmatites, the flesh and blood of the crust of the earth are niggardly treated. But, generally speaking the student will find pertinent and useful, well arranged and carefully presented information.

Among the multitudinousness of data there must needs be features with which a reviewer may disagree. There are also a few slips: thus it was not SEDERHOLM but SCHEUMANN who invented the term phlebite. However, these are trifles; by and large the book is remarkably free of errors, typographical and otherwise. The author should be congratulated upon the completion of a carefully executed piece of work.

TOM. F. W. BARTH

INFORMATION FOR CONTRIBUTORS

I. GENERAL

1. Papers on geochemistry should be submitted to the editors for the appropriate country or language (*Papers on cosmochemistry should be sent to Prof. F. A. Paneth, F.R.S.*). Papers submitted for publication will naturally be judged from the standpoint of scientific originality and novelty. Technical details of apparatus used in scientific investigation can, however, be presented in brief notes. Critical comments or preliminary results requiring early publication should be submitted as letters to the editors. Where possible, letters should be confined to 500 words. The preparation of progress reports and review articles will be invited by the editors from time to time. The journal appears as independent and complete numbers, which are combined into volumes of about 300 pages.

2. Only papers which have not been previously published can be accepted. Authors must agree not to publish elsewhere a paper submitted to and accepted by *Geochimica et Cosmochimica Acta*.

3. Fifty reprints of each paper are provided free. Additional copies can be purchased if ordered at the time the first proofs are returned.

II. SCRIPT REQUIREMENTS

1. Scripts must be written in one of the three official languages—English, French, or German.

2. The script should be typed (not a carbon copy). The text must be ready for printing and should be carefully checked for errors. Authors will receive proofs for correction.

3. Illustrations should accompany the script, mounted on separate sheets. Line diagrams that require to be redrawn should include all relevant details. Half-tone illustrations should be restricted to the minimum necessary. Photographs should be enlarged sufficiently to permit their clear reproduction, and if words or numbers appear on them, two copies should be sent, one clearly printed and the other without inscription. All illustrations should be provided with descriptive legends, which should be given on a separate sheet.

4. References in the text should be given by quoting the author's name and year of publication, i.e. AHRENS (1952). **Full references should be listed at the end of each paper, in alphabetical order, in the following manner:**

AHRENS L. H. (1952) *Geochim. et Cosmochim. Acta* **2**, 168.

and should include the standard abbreviated title of the journal, year, volume number, and page number.

5. The text of articles submitted should be concise and in a readily understandable style. The technical description of the methods used should only be given in detail when such methods are new. The essential contents of each paper should be briefly recapitulated in an abstract in English. Such an abstract may, however, be submitted by the author in the language of the original typescript for translation into English by the editorial staff.

6. To conserve space authors are requested to mark less important portions of the paper (such as description of methods, record of experimental results, etc.) for printing in smaller type.

Irradiation Colours and Luminescence

A Contribution to Mineral Physics

By Dr. Karl Przibram
Emeritus Professor of Physics at the University of Vienna

Translated and revised in collaboration with the author
By John Espenett Caffyn
Lecturer in Physics, Durham Colleges in the University of Durham

In his book *Verfärbung und Lumineszenz*, Professor Przibram provided an extensive treatment of colouration in minerals, and the luminescence which is associated with it. Due to the author's familiarity with the work carried out in Vienna and Göttingen, it was perhaps considered more thoroughly than the work carried out elsewhere, but Professor Przibram omitted no important work in the field, notwithstanding the difficulty experienced in obtaining recent Russian literature.

In the translation, Dr. Caffyn took the opportunity of revising the text, and some 500 additional references were added. Professor Przibram provided new material to make *Irradiation Colours and Luminescence* a completely up-to-date critical survey, and the only recent book which describes the colourations and luminescence produced by exposure to ionizing radiation of both natural and synthetic crystals.

In this book the mineralogist will find how far present-day physical methods will explain some of the phenomena puzzling to mineralogists: the physicist, interested in the solid state, may be assisted to a better understanding of the nature of imperfect crystals.

Ample scope for further studies is provided in the extensive references in the text and the 49 pages of bibliography.

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